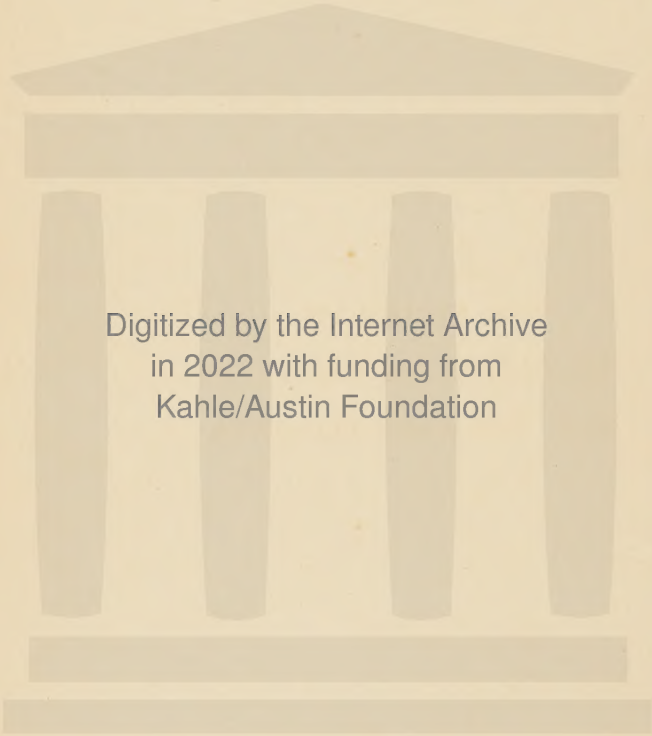
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A SYSTEM OF QUALITATIVE ANALYSIS FOR THE RARE ELEMENTS

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TORONTO

A SYSTEM

OF

QUALITATIVE ANALYSIS

FOR THE RARE ELEMENTS

BY

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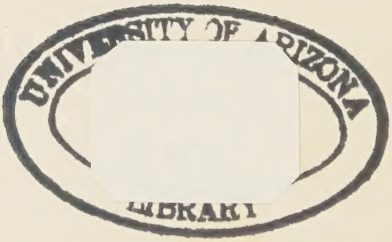

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PREFACE

In this book are presented the results of an experimental investigation, carried out during the past thirty years by the authors with the aid of a large number of their associates, research assistants, and graduate students, first at the Massachusetts Institute of Technology and later at the California Institute of Technology and the University of California. As a result of this investigation there has been worked out in detail a system of qualitative analysis that includes nearly all the metal-forming elements and makes possible their detection when present in quantity as small as one or two milligrams even when associated with other elements.

The great importance, both from industrial and scientific standpoints, of many of the "rare elements"—so called often only because of their traditional and somewhat arbitrary exclusion from the usual schemes of qualitative analysis—has made highly desirable a systematic and reliable method for their detection. Any chemist who, without previous experience in this field, has had occasion to analyze for these elements will appreciate how difficult the problem has been.

It is hoped that the existence of this System of Analysis will lead to the discovery of rare elements in minerals and ores where they have not been previously detected, and that the methods of separation here presented may assist in the purification of preparations of rare elements and may suggest improved methods for their quantitative estimation.

This publication has three purposes in view. The first is that already indicated—to supply the chemical analyst, as is done in Part I of the book, with a system of procedure which will enable him to detect the various elements in all their combinations by as simple a process as possible.

The second purpose is to record briefly, as is done in Part II of the book, the numerous experimental investigations that have been carried out in developing this System of Analysis. This part of the book is of the nature of a research monograph. The authors may perhaps mention that there is recorded concisely in these

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pages an amount of experimental material which, if presented in journal articles of the usual discursive type, would fill a large volume.

The third purpose is to provide for students a course in advanced inorganic chemistry that will afford them an acquaintance with the chemical properties of the rarer elements, many of which have now become highly important in industry, in analytical practice, and in scientific research. Suggestions to teachers or students as to ways in which the analytical scheme may best be approached and as to desirable collateral study of the rare elements are presented in an introductory section entitled The Course of Study.

At the end of the book in Appendixes are added several tables which afford much information helpful to the analyst and student. Of these may be specially mentioned the table on the "Reactions of the Elements," which has been compiled by the authors on the basis of their experience and the existing literature. Though it doubtless contains errors, it is hoped that it will be useful for reference.

The authors will be greatly indebted to anyone who will bring to their attention any difficulties met with in using the System of Analysis or errors found to exist in the text.

JULY, 1927.

ACKNOWLEDGMENTS

It is not possible for the authors to give adequate detailed recognition to the many persons who have cooperated with them in the development of this System of Analysis. This is especially true of those who took part in its early stages—men who often did the pioneer work on the analysis of separate groups, but whose processes have as a result of added experience since been greatly modified or replaced. Reference has, however, been made at the beginning of each group to the men who had the largest share in the experimental work upon it, either in its earlier or later stages. In addition, the authors desire to acknowledge the assistance of many others who made important contributions to the investigations. The following is an alphabetical list, incomplete the authors fear, of the persons who have participated in this undertaking, together with their present positions.

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The investigations have been greatly aided on the financial side by grants from the American Academy of Arts and Sciences, from the Carnegie Institution of Washington, and from the research funds of the Massachusetts Institute of Technology and the California Institute of Technology.

Without attempting to mention the many isolated journal articles, the authors would state that they have been especially

helped by the monographs of Meyer and Hauser on "Die Analyse der seltenen Erden und der Erdsäuren" (1912) and of Gooch on "Methods in Chemical Analysis" (1912), and by the papers of Mylius and his associates on the platinum elements in the Berichte der deutschen chemischen Gesellschaft, and those of Leidié and of Leidié and Quennessen on the same elements, especially in relation to the sodium peroxide fusion, in the Bulletin de la Société Chimique (1901–1902).

It may finally be mentioned that various scientific societies and journals have from time to time during the long course of these investigations received communications from the authors as to separate parts of the System of Analysis in its then state of development. A provisional detailed scheme for the preparation of the solution and for the analysis of the tungsten and tantalum groups was published in the Technology Quarterly in 1903–1904 (vol. **16**, pp. 93–131; vol. **17**, pp. 214–257). An outline of the earlier parts of the System of Analysis was presented before the International Congress of Applied Chemistry at Berlin in 1903 and published in the Zeitschrift für Electrochemie (vol. **9**, pp. 839–840). A detailed publication, which included all the common elements, but only a few of the rarer ones, made in part in association with Dr. E. B. Spear, appeared in the Journal of the American Chemical Society in 1907–1909 (vol. **29**, pp. 137–205; vol. **30**, pp. 481–563). A brief presentation of the system in outline was made before the Section of the American Chemical Society at Chicago (in 1915 in connection with the award of the Willard Gibbs Medal) and before the American Association for the Advancement of Science at Los Angeles in August 1922; also at the Dedication of the Sterling Chemical Laboratory at New Haven in April 1923. The outline, as given at the latter place, was published in 1924 in Chemical Reviews (vol. **1**, pp. 277–295).

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THE COURSE OF STUDY

THE COURSE OF STUDY

Any one undertaking the study and execution of this System of Analysis should have previously had a course in the qualitative analysis of the common elements which included analyses of unknowns with estimation of quantities and a study of the theoretical principles involved, as in A. A. Noyes' "Qualitative Analysis." He should have had at least a year's work in quantitative analysis, and should know the manipulative devices of qualitative analysis, since exact manipulation is essential. He should also be familiar with the periodic system in its modern form (see Appendix VI, page 504).

It is suggested that the subject be taken up in the following way.

Read the Introduction (pages 9–11). Read Tabular Outline I (page 8), which shows the separation of the elements into groups. Study carefully the first part of that Outline—through the precipitation of the tellurium and copper groups.

Make up a mixture containing 10 mg. each of selenium, tungsten, platinum, thallium, and tellurium; using for this purpose the test-solutions (see Appendix II, page 488), which contain 10 mg. of the element per cubic centimeter. Add to this mixture 10 cc. of 9 n. HBr; and treat it by Procedures 4, 21, 5*B*, 6, 61, 70, and 71.—Observe and record the effects resulting from each operation. Write the equations expressing all the chemical changes undergone by each of the elements present. List the other elements which, if present, would be isolated with each of those actually in the solution. If the subject is taken in class, review the separation into groups in conference with the instructor (who may with advantage introduce this topic by a demonstration-lecture, in advance of the students' work upon it).

Now, study and experiment with the successive groups, devoting enough time to each to become thoroughly familiar with it. Before considering the Procedures in detail or carrying

them out in the laboratory, understand fully the main features of the group analysis and the chemistry involved in it.

To this end first study the Tabular Outline and read the General Discussion of the group under consideration. Then make up from the test-solutions (see Appendix II) a mixture containing 10 mg. of each rare and common element of the group, as directed in the footnotes to the first or second Procedure of that group. (See pages 64, 82, 98, 113, 122, 133, 157, 175, 206, 221, and 255.)

Analyze this mixture carefully; taking time to understand the purpose and result of each operation. In doing so the following plan may with advantage be pursued:

Study the Notes on each Procedure while carrying it out.

Record in systematic form (not discursively) any effect observed with each reagent added, and state briefly what effect would be produced by each rare element separately, trying when necessary control experiments with known amounts of the separate elements.

Write all chemical equations relating to reactions undergone by each of the rare elements. (Note that the chemistry of the process is usually indicated in the Tabular Outlines.)

After making the final test for each element estimate the quantity of it there obtained by applying this final test (under just the same conditions) to 10 mg. of the element taken directly from the test-solution.

Reserve all the final tests.

Analyze by the same process an unknown mixture of this group, which should contain only 1 to 3 mg. of certain rare elements with 10 to 100 mg. of other rare elements and 10 to 300 mg. of certain common elements. Compare the final tests with those given directly by known quantities of the test-solutions. Report the number of milligrams of each element estimated to be present in the given mixture.

The following plan of supplementary study may with advantage be pursued.

Study in Appendix IV on "Reactions of the Elements" (pages 492–502) and in Treadwell-Hall's "Qualitative Analysis" the chemical properties of the various valence states of each of the rare elements involved in the group under consideration. Besides

the properties recorded in the table of "Reactions" note any reactions that are commonly used for the analytical separation or detection of the elements. When time is available, try experiments illustrating a few of the characteristic reactions of these elements with small known quantities of them. Also read in the larger text-books of inorganic chemistry, such as that of Roscoe and Schorlemmer, the sections on the rare elements involved, so as to gain broader familiarity with their history, chemical behavior, and technical importance. Refer to Ephraims "Inorganic Chemistry" (translated by Thorne) when readable discriminating surveys of various types of inorganic compounds and reactions are desired. Consult the larger hand-books of Abegg, of Gmelin-Kraut, of Friend, and of Mellor, or Chemical Abstracts, when further information as to specific compounds or reactions is needed. Refer to the corresponding Confirmatory Experiments in Part II of this book (pages 271–479) for tests of the Procedures and experiments substantiating the statements in the Notes.

Look up the position of each of these rare elements in the Periodic Table (see page 504), noting the elements of the same periodic group that precede and follow it, and those of the same row to the left and right of it. Make a table in which the characteristic reactions of the so-related elements are tabulated side by side with those of the rare elements under consideration.

After completing in this way the analysis of any group there may be discussed in conference with the instructor not only the reasons for the operations, but the principles involved (solubility, complex formation, and other mass-action effects, oxidation or valence changes, periodic-law relations, etc.).

Study and analyze in this way as many of the analytical groups as time permits. If the time is limited, it is suggested that the selenium, osmium, tantalum, thallium, and rare-earth groups (and, if need be, the alkali group) be omitted, as these are either less instructive or important or especially elaborate.

After the analysis of the various groups has been completed, study and work through in a similar way the Preparation of the Solution (Procedures 1–11). Study Tabular Outline II (page 12), and read the General Discussion (pages 13–23). Use for the laboratory work the following solid materials, continuing the operations till complete solution has resulted, or further when so indicated.

1. Mixture of pyrite (FeS_2) and stibnite (Sb_2S_3). Carry the mixture through to the end of Procedure 7.

2. Orthoclase ($KAlSi_3O_8$). Begin with Procedure 3.

3. Garnet ($Ca_3Al_2Si_3O_{12}$). Begin with Procedure 3.

4. Tungsten-steel (omitting Procedure 3).

5. Mixture of monazite sand (rare-earth phosphates) and emery (Al_2O_3).

6. A platinum-metal ore, mixed with 5 mg. of osmium and 5 mg. of ruthenium in the form of their test-solutions (to illustrate the behavior of these elements in Procedure 5). Carry the analysis through to the end of the tellurium group.

Finally carry out a number of complete analyses of solutions and of solid materials of composition unknown to the analyst, prepared by mixing pure substances in known proportions.

PART I

THE SYSTEM OF ANALYSIS

TABULAR OUTLINE I

SEPARATION OF THE ELEMENTS INTO GROUPS

Distil the material with 9 n. HBr (P. 4).

Distillate: SELENIUM GROUP: Se, As, Ge, bromides. — See T. III. (*P. 21–25.*)

Residual liquid. *Evaporate to fuming with HNO_3 and $HClO_4$ (P. 5).*

Distillate: OSMIUM GROUP: Os, Ru, tetroxides. — (*P. 5.*)

Residue. *Add 12 n. $HCHO_2$, boil (P. 6).*

Precipitate: See T. II.
TUNGSTEN GROUP: Sb, Sn, W, *Mo, ‡V, ‡Te, as oxides or phosphates.
TANTALUM GROUP: *‡Ti, Ta, Cb, ‡Zr, ‡Bi, as oxides or phosphates.
GOLD GROUP: Hg, Au, Pt, Pd, ‡Ir, ‡Rh, as metals.
— See T. IV–VI. (*P. 30–40; 41–49; 51–57.*)

Filtrate. *Evaporate, add HBr (P. 61).*

Precipitate: THALLIUM GROUP: Ag, Tl, *Pb, as bromides. — See T. VII. (*P. 61–63.*)

Filtrate. *Adjust hydrogen-ion concentration, saturate with H_2S (P. 70–71).*

Precipitate:
TELLURIUM GROUP: Te, Mo, Ir, Rh, as sulfides.
COPPER GROUP: Pb, Bi, Cu, Cd, as sulfides.
— See T. VIII. (*P. 72–78; 81–86.*)

Filtrate. *Test a portion for* IRON *and* PHOSPHATE (*P. 91*). *To rest add $NH_4C_2H_3O_2$ and $Fe(NO_3)_3$, boil, filter (P. 92). To filtrate add NH_4OH and H_2S, filter (P. 96).*

Precipitates, as hydroxides, sulfides, or phosphates:
GALLIUM: Ga.
ALUMINUM GROUP: Cr, U, V, ‡W, Al, Zn, Be.
NICKEL AND ZIRCONIUM GROUPS: Mn, ‡Zn, Co, Ni, In, Zr, Hf, Ti.
RARE-EARTH GROUP: Sc, ‡In, Th, Ce, La subgroup, Y subgroup.
— See T. IX–XII. (*P. 93–97; 101–116; 121–134; 141–149.*)

Filtrate. *Evaporate, add $(NH_4)_2CO_3$ and C_2H_5OH (P. 151).*

Precipitate: ALKALINE-EARTH GROUP: Ba, Sr, Ca, Mg, as carbonates. — See T. XIII. (*P. 151–158.*)

Filtrate: ALKALI GROUP: Na, Li, K, Rb, Cs. — See T. XIV. (*P. 161–170.*)

INTRODUCTION

The System of Analysis is presented in the form that seems best adapted to the purpose of the analyst. The presentation is primarily divided into a series of chapters, as shown in the preceding Table of Contents. The first chapter describes the preparation of the solution, and incidentally the isolation of certain groups of elements; and each of the later chapters is devoted to the analysis of the separate groups, that is, to the separation and detection of the elements precipitated by a group-reagent. The elements belonging to the various groups will be seen by reference to the Table of Contents, and the operations by which these groups are actually isolated are shown diagrammatically in Tabular Outline I on the opposite page.

At the beginning of each chapter is given a Tabular Outline (designated in references by the symbol T.). This affords a general survey of the main operations and of the chemical changes involved in the analysis of the group under consideration. These Tabular Outlines should always be carefully studied before reading the General Discussion which immediately follows them, and especially before proceeding to carry out the scheme of analysis in the laboratory. (See the Course of Study, pp. 3–6.)

In the Tabular Outlines signs are attached to the symbols of certain elements. These signs have the following significance.

> The sign * signifies that a large part, but not all, of the element will be found here when a large quantity is present.
>
> The sign † signifies that the smaller part of an element which divides itself will be found here.
>
> The sign ‡ signifies that some or all of the element may be found here when associated with certain other elements.
>
> When no sign is attached to the symbol, it denotes that some or all of the element will be found here unless it has been carried down completely at some other point (indicated by a double dagger ‡) because of its being associated with some other element.

In the General Discussions (denoted for short by D.) are presented a fuller outline of the process, the research aspects of the problem, and the considerations which led to the adoption of the various methods of separation and detection; also an account of

various collateral processes which were investigated, but not finally incorporated in the System of Analysis.

The General Discussion is followed by the Procedures and Notes (abbreviated in references to P. and N.). In the Procedures the operations are described in much detail; for careful attention to details is often essential to securing delicacy in the tests. Moreover, it is desired to make the scheme effective in the hands of chemists having little experience with the rare elements. Before analyzing unknown substances, any one using for the first time the method of analysis for any group should apply it to a known mixture containing five to ten milligrams of each element, in order that he may become familiar with the process and with the behavior of the elements. (See the Course of Study, p. 3.)

In the Procedures the directions are commonly given in the form applicable to the case where all elements that could be present are present, the modifications admissible when certain operations lead to negative results being usually sufficiently evident.

In the Notes are described the reasons for the detailed operations, possible modifications of them in special cases, the behavior of the various elements, and the application to them of the theoretical principles involved. It is assumed, however, that the principles themselves are known, and that the reader is familiar with their application to the common elements, at least to the extent covered by A. A. Noyes' Qualitative Analysis. The theoretical explanations of the behavior of the common elements are therefore not reproduced here.

A separate Part of the book, given at the end of the System of Analysis so as to avoid interrupting the analytical procedures, consists of Confirmatory Experiments (C. E.). In this Part are presented in detail the results of the researches made in developing the scheme of analysis. The Confirmatory Experiments serve to justify the Procedures adopted, and to substantiate the statements made in the Notes. They will present to the critical reader the experimental evidence on which the conclusions are based; and they may prove of interest to other investigators in inorganic and analytical chemistry. The experiments deal, to be sure, largely with the application of the known facts of inorganic chemistry to specific analytical processes; yet among them are included the results of many new lines of investigation. Taken as a whole, they

afford, it is believed, a vast amount of detailed analytical information which is not gathered together elsewhere.

This Part on the Confirmatory Experiments is subdivided into chapters corresponding to those of the System of Analysis; and the separate experiments are so arranged and numbered as to facilitate reference to them from the General Discussion, Procedures, or Notes to which they relate. References are also given to the previous work of others in cases where an analytical separation not in common use has been adopted which has been developed by particular investigators, or in cases where published work furnishes detailed evidence of some feature of the process employed. In general, however, it has been found entirely impracticable to give anything like complete references, in view of the huge mass of publications bearing on a scheme of analysis like the present. None the less do the authors recognize that the structure is based on the foundations that have been laid by a multitude of other investigators.

Of the more special features of the System of Analysis mention may be made of the following.

The scheme is worked out for the case that not more than 500 milligrams of any one common element are present, and that not more than 100 or 200 milligrams of any one rarer element are present; hence care must be taken to use for the analysis not more of the original material than probably contains such quantities.

The process enables in most cases one milligram or less of any element to be detected when carefully executed by a skilled manipulator who also has already acquired reasonable familiarity with the scheme; but in certain combinations the limit of detection of some elements may rise to two, or perhaps three milligrams. With elements of very low equivalent weight, such as lithium or beryllium, considerably less than one milligram (but usually not proportionally less) can be detected.

When it is directed to add a variable quantity of a reagent (for example, 5–15 cc.), the amount used should be adjusted to the size of the precipitate or residue.

The term normal (n.) is in this book always used in a metathetical, never in an oxidizing sense. Where its significance would be doubtful, the term formal (f.) is used, denoting formula-weights per liter.

Tabular Outline II

Preparation of the Solution. Isolation of Osmium, Selenium, Tungsten, Tantalum, and Gold Groups

Boil the material with 10 cc. of 9 n. HBr; add Br_2 and heat (P. 2).

Filtrate: all elements as bromides.

Residue. *Digest with HF, fume with $HClO_4$, evaporate almost to dryness (P. 3).*

Residue: perchlorates, oxides, unattacked material.

Vapor: SiF_4.

Unite, boil down to 3 cc., collecting distillate in water (P. 4).

Distillate: SELENIUM GROUP Se, As, Ge, as bromides. *Analyze by P. 21–25.*

Residual liquid. *Evaporate with HNO_3, distil (P. 5).*

Distillate: OsO_4. *Absorb in NaOH*

Orange color: Na_2OsO_5-H_2O.

Residual liquid. *Add 9 n. $HClO_4$, evaporate to fuming, distil (P. 5).*

Distillate: RuO_4. *Absorb in NaOH.*

Orange to red color: Na_2RuO_5-H_2O. *Add C_2H_5OH.*

Black precipitate: Ru_2O_{3-4}.

Residue. *Add 12 n. $HCHO_2$, boil (P. 6).*

Residue: oxides of tungsten and tantalum groups, gold-group metals, AgBr, sulfates of Pb, Ca, Sr, Ba, Cr, other unattacked material. *Digest with HF, dilute (P. 7).*

Filtrate. *Analyze for all other groups.* See T. I.

Filtrate: TUNGSTEN GROUP Sb, Sn, W, Mo, TANTALUM GROUP Ta, Cb, Ti, as fluorides. *Analyze by P. 30–49.*

Residue: gold-group metals, AgBr, PbF_2, CaF_2, SrF_2, $BaSO_4$, $Cr_2(SO_4)_3$, unattacked material. *Boil with Na_2CO_3 solution, filter; reject filtrate; treat residue with $HClO_4$ (P. 8).*

Residue: gold-group metals, AgBr, unattacked material. *Heat with HNO_3 and HCl, filter. Extract residue with NH_4OH (P. 9).*

Filtrate: Pb, Ca, Sr, Ba. *Analyze for these elements.*

Filtrate: GOLD GROUP Hg, Au, Pt, Pd. *Analyze by P. 51–57.*

Extract: $Ag(NH_3)_2Cl$. *Add $HC_2H_3O_2$.*

Precipitate: AgCl.

Unattacked material.

NONMETALLIC: oxides of Al, Cr, Ti, Zr, Sn; phosphates of Ti, Zr, Th, Ce, . . .; various silicates; sulfates of Cr, Ba; ThF_4, CaF_2; C, Ir, Rh. *Fuse with $K_2S_2O_7$ (P. 10).* See T. IIA.

METALLIC: precipitated Ir, Rh; platinum alloys; alloys of Fe, Si, Cr, W. *Fuse with Na_2O_2 (P. 11).*

PREPARATION OF THE SOLUTION

Tabular Outline II

See page 12.

General Discussion

Acknowledgment.—In the development of the Preparation of the Solution we have been ably assisted by G. Victor Sammet, Julius E. Ober, Isoburo Wada, L. Merle Kirkpatrick, and Donald L. Loughridge.

D. 1. Principles relating to the Choice of Solvents.—A primary feature of any system of analysis for all the elements must be a general process for the preparation of a solution of the material to be analyzed. The method of procedure here presented has been worked out with the aim of developing a systematic method which is rapid in its application to materials commonly met with, which is so general and complete as to effect the solution of nearly all substances, which provides against the loss of volatile elements, and which lends itself to sharp and convenient group separations in the subsequent analysis.

Any complete procedure for preparing the solution naturally includes treatment of the material with solvents of the following types: (1) with a strongly acid solvent, so as to dissolve basic oxides and salts of weak acids; (2) with a powerful oxidizing solvent, to dissolve metals and sulfides; (3) with hydrofluoric acid, to volatilize silica and decompose silicates not acted on by the ordinary acids. In selecting the solvents, determining the order in which they are applied, and prescribing the experimental conditions, account must be taken especially of the facts: (*a*) that in certain valence states some elements (arsenic, germanium, selenium, osmium, ruthenium) volatilize out of boiling solutions; (*b*) that certain other elements (tantalum, columbium, tungsten) will not remain in solution in dilute hydrochloric, nitric, or sulfuric acid, and must therefore be isolated early in the process; and (*c*) that sulfuric acid, if added as a solvent or produced by the oxidation of sulfides, causes precipitation of several elements (barium, strontium, calcium, and lead; also chro-

mium, if the acid is fumed). These conditions permit, however, of several combinations in the selection and order of application of the solvents.

In case the material contains organic matter, this is destroyed at the start by perchloric and nitric acids—a process whose advantages are considered in D. 13.

D. 2. Advantages of First Using a Halogen Acid.—The first operation in the adopted process is the treatment of the substance with concentrated hydrobromic acid. Hydrobromic and hydrochloric acids have over nitric acid the following advantages: (1) They have a more powerful acid solvent action on basic oxides and basic salts, like those of iron, aluminum, antimony, tin, and titanium; this being probably due to their tendency to form complex or slightly ionized halides. (2) As the initial solvent, when used hot and concentrated, either of the halogen acids decomposes most sulfides with liberation of the sulfur in the form of hydrogen sulfide, instead of converting it into sulfuric acid and thereby causing precipitation of insoluble sulfates. (3) These acids dissolve, because of their reducing action, a few substances, such as manganese and lead dioxides and lead chromate, which are not attacked by nitric acid. (4) They do not convert osmium into its volatile tetroxide.

The halogen acids have the effect, to be sure, of forming volatile halides with trivalent arsenic, quadrivalent selenium, and germanium; and these elements volatilize largely or completely when their solutions in halogen acids are boiled or otherwise evaporated. The loss of these elements can, however, be avoided by carrying out the digestion in a flask connected with a reflux condenser, and then evaporating in a distilling flask and collecting the distillate, as is done in the process here adopted.

D. 3. Treatment of the Material with Hydrobromic Acid and Bromine (P. 2).—Hydrobromic acid, rather than hydrochloric acid, is employed for the reason that on boiling the solution there results a distillate containing a group of volatile elements, called here the *selenium group,* comprising the three elements, selenium, arsenic, and germanium. For hydrobromic acid causes arsenic and selenium to distil over almost completely in their lower valence states, even when originally present in the higher valence states; while with hydrochloric acid quinquivalent arsenic volatil-

izes scarcely at all, and selenium even when quadrivalent only slowly and incompletely. This process has the advantage of eliminating these volatile elements at the start in the form of a fairly well defined, readily analyzed group. The process is similar to that used by Gooch [1] and his associates for separating selenium from tellurium and arsenic from antimony.

If the material does not dissolve on warming it with the hydrobromic acid, the mixture is made strongly oxidizing by the addition of liquid bromine. The bromine serves to dissolve most of the metals and sulfides that are not attacked by hydrobromic acid.

D. 4. Treatment of the Unattacked Residue with Hydrofluoric Acid and Decomposition of the Resulting Fluorides (P. 3).—Any material that resists the powerful acidic, reducing, and oxidizing action of hydrobromic acid and bromine is likely to be a silicate or silica, and the residue is therefore filtered off and heated with hydrofluoric acid. The silica may be present originally as such, or be liberated from a silicate as silicic acid which is made almost entirely insoluble by the boiling concentrated acid. The distillation of the hydrobromic acid solution, which is the next step in the process, is postponed till there can be united with it the solution resulting from the fluoride treatment of the residue, since this may contain selenium-group elements. Instead of filtering out the residue and treating it with hydrofluoric acid, the whole mixture might be evaporated and so treated; but this, though simpler from a manipulative standpoint, is not advisable for the reason that calcium, thorium, and rare-earth elements, which form fluorides that are only slowly decomposed by the fuming perchloric acid later used for the purpose, are often removed from the residue by the treatment with the hydrobromic acid. Another reason for making it the general procedure to filter out any unattacked residue before distilling off the hydrobromic acid is that in the absence of silicate there may be no residue to treat at that point, while a non-silicious residue, consisting of various other substances (see D. 7 and 8) that are dissolved by the concentrated acid, may separate after the acid is removed, thus making it impossible to determine whether a silicious residue requiring fluoride treatment is present.

The problem of decomposing the fluorides was one that re-

[1] Gooch, *Methods in Chemical Analysis*, 316, 390 (1912).

quired extended investigation. This decomposition is commonly effected by heating them with sulfuric acid to the fuming point; but the use of this acid has the serious disadvantage in systematic qualitative analysis that it yields, as a residue slightly soluble in water, the sulfates of lead, barium, strontium, calcium, and chromium. Evaporation with nitric acid, even many times repeated, decomposes very incompletely calcium, thorium, and rare-earth fluorides when present in large quantity. It was found, however, that fuming perchloric acid attacks these fluorides much more rapidly; and its use was adopted as part of the process for the preparation of the solution. When the fuming is continued for ten or fifteen minutes, this acid decomposes completely even a large quantity of any of these fluorides (except that a little thorium fluoride may remain). The resulting perchlorates, after evaporating off most of the free perchloric acid, are united with the main hydrobromic acid solution.

It need hardly be said that this method of decomposing silicates is far more satisfactory in qualitative analysis than fusion with sodium carbonate; for it is more rapid, does not introduce alkali elements, and at once eliminates silica by volatilization as silicon fluoride. The extent to which hydrofluoric acid is generally effective in decomposing silicates was studied by heating a large number of silicate minerals with this solvent. Only a few types were found which resisted it, such as cyanite (Al_2SiO_5), beryl ($Be_3Al_2Si_6O_{18}$), zircon ($ZrSiO_4$), and tourmaline.

D. 5. Distillation with Hydrobromic Acid. Isolation of the Selenium Group (P. 4).—The next step in the adopted process is to distil the hydrobromic acid solution and collect the distillate in water. The separation of the selenium-group elements from other elements by this operation is fairly sharp, provided the boiling be discontinued when about 3 cc. of the acid remain in the distilling flask. Selenium, arsenic, and germanium then pass nearly completely into the distillate. Only about 5 mg. of arsenic when 500 mg. are present, and 1.5 mg. of germanium when 25 mg. are present, are left in the residual liquid; and of other elements tin and antimony are the only ones that pass into the distillate in appreciable quantity (about 8 mg. of tin and 2–5 mg. of antimony when 500 mg. are present). No osmium or ruthenium distils over as the volatile tetroxide, since these elements are kept

in lower valence states by the reducing action of the hydrobromic acid. Mercury does not volatilize because its bromide is firmly bound in the form of a complex acid.

Experiments were made to determine the best point at which to break the hydrobromic acid distillation, with the view of securing as sharp a separation as possible of the volatilizing elements from those remaining behind. Two other plans were specifically investigated: first, evaporating the remaining 3 cc. of hydrobromic acid almost completely (down to a volume of about 0.5 cc.) by immersing the flask in a boiling water-bath and passing through it a rapid current of air; and second, adding 3 cc. of 9 n. perchloric acid and heating the flask in a paraffin bath till the temperature of the heated liquid rose to 130–140° when substantially all the hydrobromic acid was expelled.[1]

The experiments showed that when the evaporation is carried to 0.5 cc. substantially all the arsenic (all but 0.5 mg. out of 500 mg.) is volatilized, and that 200 mg. of tin and 15 mg. of antimony pass over when 500 mg. are present, while mercury, osmium, and ruthenium are still completely retained. The fact that tin divides itself so nearly equally between residue and distillate, and that even antimony divides somewhat, seemed a sufficient reason for abandoning this process. The experiments on the second process, in which the hydrobromic acid is boiled off by heating with perchloric acid in a paraffin bath to 130–140°, showed that 200 mg. of tin, 25–30 mg. of antimony, and 2–3 mg. of mercury pass into the distillate when 500 mg. are present; but that ruthenium and osmium are still completely, or nearly completely, held back. This process is evidently even less satisfactory than the first one.

D. 6. Distillation with Nitric Acid and Perchloric Acid. Isolation of Osmium and Ruthenium (*P. 5*).—The next operation is the distillation of the residual solution first with nitric acid and then with perchloric acid. While the main purpose of these operations is, as described in D. 7, the conversion of the bromides into perchlorates and oxides, yet it causes also the two elements osmium and ruthenium, because of the volatility of their tetroxides, to escape from the boiling solution. As already stated, these

[1] For the detailed experiments on the first process, see C. E., P. 4, Notes 2, 3; for those on the second process, see C. E., D. 16 in the columns of the table headed "preliminary evaporation."

elements do not volatilize during the distillation with hydrobromic acid, since this acid reduces them to lower valence states; but the nitric acid added destroys the remaining hydrobromic acid and oxidizes the osmium to tetroxide, which vaporizes when the distillation is resumed. When the mixture is heated to fuming with perchloric acid, ruthenium also oxidizes and distils over as the tetroxide. These treatments are therefore carried out in a distilling flask, and the vapors are led into successive portions of sodium hydroxide solution, to absorb the tetroxides of osmium and ruthenium, which can then be readily tested for.

Although the removal of osmium and ruthenium is an incidental feature of the preparation of the solution, yet this distillation process of separating them from other elements and from each other is a simple and effective one, and constitutes probably the best method of isolating and detecting these elements. The volatilization of osmium from boiling nitric acid solutions has long been employed for the separation of this element. Ruthenium has also frequently been distilled over with the help of permanganate or chlorate added to an acid solution, or by passing chlorine through an alkaline one; but these processes introduce other base-forming elements into the solution. The discovery by Dr. E. H. Swift at the California Institute that perchloric acid at its fuming point will oxidize ruthenium to its tetroxide made it possible to remove immediately this element, along with osmium, from the acid solution of the original material.

D. 7. Isolation of the Tungsten and Tantalum Groups by Evaporating with Perchloric Acid and Diluting. Partial Removal of Alkali Elements (P. 6).—The main purpose of the evaporation with nitric and perchloric acids is to decompose all bromides present as completely as possible, so as to cause, when the perchloric acid is diluted, the separation as oxides of a large number of elements, some of which are precipitated either not at all or incompletely when halides are present. These elements are antimony, tin, tungsten, and molybdenum (constituting the *tungsten group*), and titanium, tantalum, and columbium (constituting the *tantalum group*).

Five of the elements of these groups, namely, tantalum, columbium, tungsten, antimony, and tin, are precipitated completely enough for analytical purposes (except in a few combinations

with other elements) when the strongly fumed perchloric acid is diluted and heated to boiling. Furthermore, any molybdenum in excess of 2 or 3 mg., and any titanium in excess of about 4 mg., are ordinarily found in the residue.

When phosphate is also present, not only all of the titanium, but all of the zirconium may be precipitated here. Moreover, vanadium may be partly or wholly carried out with tin when they are simultaneously present, and tellurium and bismuth may be precipitated with other elements. Provision must therefore be made for the detection of these five elements, as well as for phosphate, in the analysis of the tungsten and tantalum groups.

The perchlorates of potassium, rubidium, and cesium may also be in the residue filtered from the hot perchloric acid when a large quantity of these alkali elements is present; but these are removed by washing with boiling water, and are united with the filtrate. When this filtrate is cooled, these perchlorates separate to a large extent, and are filtered out. Their removal is advantageous, since otherwise they would come out with the alkaline-earth group when it is precipitated from a small volume of solution by ammonium carbonate and alcohol.

The perchloric acid solution is analyzed for all metal-forming elements except those which already have been completely removed.

D. 8. Precipitation of the Gold Group by Evaporating with Perchloric Acid and Boiling with Formic Acid (*P. 6*).—The fumed perchloric acid solution might be diluted with water, so far as the separation of the tungsten and tantalum groups is concerned; but, in order to attain certain other results which simplify the later procedures, 12 n. formic acid is added instead of water, and the mixture is boiled with this reagent. This causes complete precipitation in the metallic state of the four elements, mercury, gold, platinum, and palladium, constituting the *gold group*. The isolation of these elements at this point might be of questionable advantage were it not that gold is almost completely precipitated, and platinum and palladium (when a large quantity is present) are likely to be partially precipitated, by the fuming perchloric acid alone.

Another reason for the use of formic acid, however, is that it reduces to a lower state of oxidation various elements, and thus

prevents their precipitation at this point or otherwise simplifies the subsequent analysis. Thus, if water is employed for the dilution, there may result the following effects not produced by formic acid: manganese is precipitated as dioxide, and vanadium as pentoxide, when these elements are present in large quantity; lead and chromium present together may yield a precipitate of lead chromate; thallium remains in the thallic state and can not be immediately afterwards removed in the form of thallous bromide; and chromium and iron are present as chromic acid and ferric salt so that they may cause the separation of much sulfur in the subsequent treatment with hydrogen sulfide.

On the other hand, the use of formic acid has the disadvantage that it may precipitate as metals with the gold group some of the rhodium and iridium; but this does not compensate its many advantages.

D. 9. Extraction of the Tungsten and Tantalum Groups from the Residue by Hydrofluoric Acid (*P. 7*).—The residue from the perchloric and formic acid treatments may therefore consist of oxides of the tungsten and tantalum groups, or of metals of the gold group, or of still unattacked material, or of all of them. It is digested with hydrofluoric acid to dissolve the oxides of the tungsten and tantalum groups, and thus separate them from the gold-group metals and from any original material still present. The solution is then subjected to the process of analysis worked out for the tungsten and tantalum groups, it being first evaporated with sulfuric acid to decompose the fluorides.

D. 10. Treatment of the Residue with Sodium Carbonate Solution (*P. 8*).—The residue from the hydrofluoric acid extraction may contain, in addition to unattacked material, the fluorides of lead, calcium, and strontium (when their sulfates were in the original material), and of bismuth (when carried down with the tungsten and tantalum groups); also silver bromide (when silver was present). All of these substances except the last would dissolve in the acids required for dissolving the gold-group metals, and thus contaminate the gold-group solution. Moreover, it is desirable to bring these compounds separately into solution so as to detect the respective elements, as well as to dissolve barium sulfate, which will be found here when it was originally present. The residue is therefore boiled with concentrated sodium carbon-

ate solution, whereby all these compounds, except silver bromide, are converted completely or nearly completely into carbonates. The sodium carbonate solution is rejected; but the residue from it is treated with perchloric acid to dissolve the carbonates, and the solution is analyzed for the elements that may be present in it.

D. 11. Extraction of the Gold Group from the Residue by Nitric and Hydrochloric Acids (*P. 9*).—Having removed by the boiling with sodium carbonate solution any fluoride or sulfate introduced by the previous treatments, the gold group is then obtained in solution by itself by treating the residue with nitric and hydrochloric acids. There is only one complication here—that arising from the fact that the iridium and rhodium that may be present, owing to their having been partially precipitated by the boiling with formic acid, are likely to divide themselves between the acid solution and the residue. This makes it necessary to provide for their detection in both these places, as well as in the main perchloric acid solution; but there seems to be no way of avoiding this.

From the residue any silver that may be present (as chloride) is then extracted by concentrated ammonium hydroxide.

D. 12. Fusion of the Unattacked Material (*P. 10, 11*).—Only rarely will any residue remain after the severe treatments to which the material has been subjected, but occasionally some undecomposed material still remains. This is likely to consist of one or more of the following substances: oxides of aluminum, chromium (as chromite, $FeO \cdot Cr_2O_3$), tin, titanium, and zirconium (as zircon, $ZrO_2 \cdot SiO_2$); phosphates of thorium and rare earths (as monazite); thorium fluoride; certain silicates not decomposable by hydrofluoric acid (such as cyanite, tourmaline, beryl); carbon or silicon carbide; precipitated rhodium and iridium, platinum alloys, and alloys of iron, nickel, chromium, molybdenum, tungsten, and silicon.

All these oxides (except that of tin) and the phosphates and fluoride are most readily brought into soluble form by fusion with the acid flux, potassium bisulfate; while the platinum metals and alloys, resistant alloys of iron with other metals, and tin oxide are most quickly dissolved by fusion with the strongly alkaline and oxidizing flux, sodium peroxide. The residue, if non-metallic, is therefore fused with the first of these fluxes; if metallic, with the

second. For the treatment in detail of a non-metallic residue, see Tabular Outline II A on p. 54.

The bisulfate process is a well known one, and requires no special mention; except to note that, now that fused-silica crucibles are available, a platinum crucible need not be used for the fusion, thereby avoiding the introduction of platinum into the analysis.

Attention should, however, be called to the extraordinary effectiveness of the peroxide fusion, which was studied by Leidié and Quennessen,[1] especially with reference to the platinum metals. These metals are all quickly converted by this powerful flux into forms soluble either in water or hydrochloric acid (except that platinum itself is partially converted into a yellow oxide which dissolves only very slowly on digestion even with concentrated acid). The fusion, to be sure, cannot be carried out in a platinum or porcelain vessel, but a nickel crucible may be employed. This metal is unfortunately much attacked, and account has to be taken of its presence in the resulting solution.

The advantages were considered of subjecting the undecomposed material to a fusion with sodium carbonate before that with the bisulfate; for there are a few silicates (such as those named above) and a few other substances (such as barium sulfate, chromite, graphite) which resist the action of hydrofluoric acid and the commonly employed acids, but are brought into soluble form by a carbonate or carbonate-nitrate fusion. However, most, if not all, of these substances are decomposed either by the bisulfate or peroxide fusion. Incidentally, the carbonate fusion would replace the boiling with sodium carbonate solution preceding the extraction of the gold group; but the boiling process is simpler in the respect that the filtrate from it contains no base-forming elements and can be at once rejected. Moreover, as stated above, it is advantageous to boil with sodium carbonate before dissolving the gold group in order to prevent various elements that may be present as fluorides from passing into the solution; and this process provides, almost as well as fusion, for the alkaline-earth sulfates, which are the substances most likely to be present. Introduction of a sodium carbonate fusion seemed therefore to be an unnecessary complication.

[1] Leidié and Quennessen, *Bull. soc. chim.*, (3), **27**, 179 (1902).

D. 13. Destruction of Organic Matter by Perchloric Acid (*P. 1*).—A novel incidental feature of this Preparation of the Solution is the plan of freeing the material from organic matter, by using perchloric and nitric acids, in place of sulfuric and nitric acids, which are commonly employed. The use of perchloric acid for this purpose has some general advantages, as well as some special advantages from the standpoint of this system of analysis for the rare elements. First, many common organic substances, such as cellulose, starch, and tartaric acid, are charred to a much less extent and more rapidly oxidized by the perchloric-nitric than by the sulfuric-nitric mixture. Second, the sulfuric treatment causes formation of slightly soluble salts of lead, barium, strontium, calcium, and chromium, which have later to be brought into solution by special processes; while the only difficulty of this kind in the perchloric treatment is the separation of potassium perchlorate, which however is readily dissolved by hot water. Third, the perchloric treatment enables, as stated above, a whole series of elements (those of the tungsten and tantalum groups) to be precipitated as oxides much more completely than is the case when sulfuric acid is present in the solution. Fourth, owing to the higher temperature required in the sulfuric process, there is greater loss of mercury. Finally, since perchloric acid has been found most suitable to employ for the preparation of the solution when organic matter is not present, the use of sulfuric acid for destroying it would make necessary extensive modifications of the regular procedures in this special case. The only objection to the use of perchloric acid is the fact that, if not properly applied, dangerous explosions may result; but experiments showed that these do not occur if the organic material is first heated with concentrated nitric and perchloric acids at the temperature of the steam-bath. The perchloric-acid treatment, on account of its many advantages, was therefore adopted.

MODIFICATIONS OF THE PROCESS INVESTIGATED

D. 14. Possible Alternative Treatment of the Material with Hydrochloric and Nitric Acids.—For dissolving the material, hydrochloric acid might be substituted for hydrobromic acid, and concentrated nitric acid substituted for liquid bromine, employing exactly the same manipulative procedure for this treatment and for the subsequent distillation as is followed (in P. 2 and P. 4) when hydrobromic acid and bromine are used. The solvent action on various substances would in general not be greatly different in the two cases. The evaporation of the hydrochloric-nitric-acid mixture to a small volume would, however, result in the complete volatilization of germanium and osmium, and in the non-volatilization of arsenic and selenium.

The facts that arsenic and selenium are not removed and that their separation and detection must be provided for in later groups (in the case of arsenic in two different groups) constitute the main disadvantages of the hydrochloric-nitric process. This process has, however, also the following minor defects. In the subsequent evaporation and boiling with perchloric acid to destroy halides mercuric chloride would be much more slowly decomposed than is mercuric bromide; and consequently, much more mercury would volatilize with the vapors, making it desirable to test for this element in the distillate (which contains also the ruthenium). Similarly, silver chloride is less rapidly decomposed by the boiling perchloric acid than is silver bromide, so that an undissolved residue would more commonly remain. Finally, since the selenium would be in the form of selenic acid, it would be precipitated only very slowly in the subsequent hydrogen sulfide treatment (unless provision were made for previously reducing it by means of boiling hydrochloric acid).

These disadvantages are not so serious as to preclude the use of the hydrochloric-nitric process; but the time saved in the earlier stages of this process is nearly or more than compensated by that involved in the later operations required for the removal and detection of arsenic and selenium. This is especially true when the very rare elements germanium, osmium, and ruthenium need not be tested for; for in this case the hydrobromic acid process of preparing the solution and the subsequent analysis of the selenium group can be much shortened, in ways that will be obvious to the analyst.

D. 15. Decomposition of Fluorides with Nitric Acid with Addition of Silica.—Before it was found that perchloric acid furnishes so satisfactory a means of decomposing insoluble fluorides and isolating the tantalum and tungsten groups, it was discovered that the decomposing action of nitric acid can be much increased by the addition of precipitated silica, doubtless owing to its removal of any liberated hydrofluoric acid by its conversion into fluosilicic acid. And as a result of a long series of experiments a fairly satisfactory process was worked out on this basis.

The process consists in detail in evaporating the hydrofluoric acid mixture with nitric acid just to dryness, evaporating twice with 5 cc. of 16 n. HNO_3 to dryness, and heating the residue to boiling with 6 n. HNO_3; then, if a clear solution has not resulted, the liquid is evaporated, 10 cc. of 16 n. HNO_3 and 1 g. of ignited precipitated silica are added, the mixture is digested on a steam-bath for an hour and then evaporated to dryness, and the residue is heated in a hot closet at 120° for an hour and finally treated with 25 cc. of 2 n. HNO_3.

The presence of the excess of silica, however, prevents determining at once whether the material has been completely decomposed, and makes necessary later an additional operation for removing it.

D. 16. Process for Volatilizing Various Elements from Perchloric Acid Solution in a Current of Steam and Hydrogen Chloride.—A long series of experiments was also made in order to determine the practicability of distilling off some of the other elements as chlorides in a current of steam and hydrogen chloride. The process of passing dry hydrogen chloride gas over the solid material heated to a fairly high temperature in a combustion tube has often been employed for quantitative analytical purposes; but this process is troublesome in its execution, and without elaborate precautions does not lend itself to the detection of small quantities. It was thought that a simple manipulative process might be developed by passing a mixture of steam and hydrogen chloride through a perchloric acid solution of the material in a distilling flask heated in a liquid bath. And in fact the following procedure was found to give fairly satisfactory results.

To the 3 cc. of hydrobromic acid solution remaining after removal of the selenium group in the 50-cc. distilling flask (having

preferably a short neck with a low side-arm) 6 cc. of 9 n. $HClO_4$ are added. A stopper carrying a tube and thermometer both extending to the bottom is inserted in the flask, and its side-arm is caused to deliver into 10 cc. of water in a graduate immersed in ice water. The flask is heated in a paraffin bath till most of the hydrobromic acid is evaporated; then the temperature of the distilling liquid is raised to 170° and maintained there, and there is passed through it for 10 or 15 minutes a rapid current of gas made by boiling off 2 cc. per minute from 100 cc. of 12 n. HCl.

It was found that by this treatment the five elements, antimony, tin, mercury, osmium, and ruthenium, passed over into the distillate in large proportion, and that by continuing the distillation 15 minutes longer these elements were under the best conditions removed so completely that not more than one milligram of any of them remained in the flask (except perhaps of osmium and ruthenium, which were not so fully studied). No other element was found to distil over, except molybdenum, of which not more than 3 mg. passed over even when 100 mg. were present. In spite of these fairly satisfactory results, the process was abandoned because of the difficulty of always realizing just the right conditions as to the rate of flow of the vapors and the temperature without employing an unduly elaborate apparatus. A higher temperature than 180° can not be used, since it results in rapid evaporation of the perchloric acid and separation of antimony in the solid state as antimonic acid, in which form it is only very slowly volatilized.

D. 17. Isolation of the Tungsten and Tantalum Groups by Evaporating with Nitric Acid and Dehydrating.—In the early stages of these researches, before it was found that perchloric acid could be used for decomposing the fluorides, a study was made of the completeness of separation of the tungsten and tantalum groups as oxides by evaporating the mixture containing them to dryness with nitric acid, dehydrating the residue by heating it at 120°, and boiling it with dilute nitric acid. The limits of separation of the various elements in general correspond strikingly with those found in the perchloric acid fuming. However, the latter method gives, probably on account of better dehydration, a more complete precipitation of molybdenum and of antimony, but a somewhat less complete one of titanium, probably because of its more basic character.

D. 18. Precipitation of Iridium and Rhodium by Boiling with Formate.—Inasmuch as more or less of the iridium and rhodium was found to be unavoidably thrown down by the boiling with formic acid, it seemed worth while to determine whether conditions might be found under which the whole quantity of these elements is precipitated by boiling for a moderate length of time with more nearly neutral formate, as has been recommended by Mylius and Dietz[1] and other investigators. If this proved to be the case, the required concentrations of formate and hydrogen-ion might be attained, without greatly modifying the general plan, by partially neutralizing with ammonium hydroxide the free perchloric and formic acids after filtering off the residue of the tungsten, tantalum, and gold groups, and boiling the mixture. The experiments, however, failed to lead to the discovery of any conditions of concentration under which the iridium or rhodium could be fairly completely precipitated except by several hours boiling. Moreover, copper and tellurium were found to be partially precipitated under these conditions. As the subjection of the main solution near the beginning of the analysis to this lengthy operation seemed clearly undesirable, the thought of using this process was abandoned.

D. 19. Process for Precipitation of the Gold Group by Metallic Silver.—Before the process of treating the mixture from the perchloric acid fuming with formic acid was adopted, a satisfactory method of separating the elements of the gold group from the elements iridium, rhodium, and ruthenium, as well as from the commoner elements precipitated by hydrogen sulfide, was worked out. As this may prove useful in other connections, especially in separating these rarer platinum elements from platinum and palladium, it will be briefly described here.

The method consists in evaporating a nitro-hydrochloric acid solution with 2 cc. of 95% H_2SO_4 till this acid begins to fume, diluting with 25 cc. of water, adding two drops of 6 n. HCl, and shaking for five minutes with successive one-gram portions of moist precipitated silver till no further darkening of the silver can be observed (adding before each shaking one or two drops more of 6 n. HCl).

[1] Mylius and Dietz, *Ber. deutsch. chem. Ges.*, **31**, 3191 (1898).

Under these conditions there is a distinct darkening of the first portion of silver when 0.5 mg. of platinum, palladium, gold, or mercury is present; and 100 mg. of the first three elements or 500 mg. of mercury are completely precipitated after three or four shakings. None of the other elements is at all precipitated; except that selenium, if present, is partially thrown down, and that a little tellurium may precipitate when much is present, especially if more than the specified quantity of hydrochloric acid is added or if the mixture is shaken with the silver longer than is necessary. Under the stated conditions no iridium, rhodium, or ruthenium is precipitated on the silver.

The silver precipitate may be analyzed as follows. It is heated with 3 n. HNO_3 to dissolve the silver, whereby the mercury and palladium and a little of the platinum also pass into solution. The solution is then diluted and treated with hydrochloric acid to remove the silver; and the filtrate is united with the solution obtained by dissolving in nitric and hydrochloric acids the residue (containing the gold and most of the platinum) from the nitric acid treatment. The solution so resulting, after proper concentration, may then be analyzed for the four elements of the gold group, for example, by the process included in this System of Analysis.

This process of separating the gold group from other elements is very satisfactory, except in the respect that the dissolving and subsequent precipitation and filtration of the large amount of silver used as reagent is troublesome. Some experiments were made to determine whether metallic mercury could be substituted for the silver (assuming that provision had been made for the previous detection of the element mercury); for the excess of mercury and the mercurous chloride resulting from its action could readily be removed from the precipitated gold, platinum, and palladium by ignition. The results indicated that the action of mercury is almost identical with that of silver, and that an excellent process for the separation of the platinum elements into two groups might be based upon its use. The process was, however, not fully tested, as there seemed to be no place for it in this System of Analysis.

PREPARATION OF THE SOLUTION

Tabular Outline II

See page 12.

Procedures and Notes

Procedure 1.—*Preliminary Examination and Preparation of the Material for Solution.*—In case the material is metallic, convert about 1 g. of it into a form that offers a large surface by hammering it in a steel mortar, filing it with a fine steel file, shaving it with a knife, or converting it into turnings in a lathe. Weigh out 0.5 g., and treat it by P. 2.

In case the material is a solution, note its odor and test it with litmus paper. Evaporate in a casserole on a steam-bath enough of the solution to yield about 2.5 g. of residue. Treat samples of this residue as described in the following paragraphs.

In case the material is a non-metallic solid, note its color, odor, and texture; examine it with a lens to determine whether it is heterogeneous, and if so, note the appearance of its constituents. Powder very finely about 2.5 g. of the material by grinding it in a mortar, using an agate one with minerals or other hard substances, till it no longer feels at all gritty.

Heat gently at first, then strongly, about 0.2 g. of this material in a hard-glass tube (about 1 cm. in bore and 10 cm. in length) closed at one end. (Blackening of the material with tarry sublimate or burnt odor, presence of ORGANIC MATTER; aqueous condensate in cool part of tube, presence of WATER.) If much organic matter seems to be present, weigh about 1 g. of the finely divided material in a porcelain crucible, ignite it strongly, placing the crucible if need be on its side, till the organic matter is burnt off, and cool and weigh the crucible.

If organic matter is thus proved absent, weigh out 1.0 g., and treat it by P. 2.

If organic matter is thus proved present, treat the finely divided material as follows. Place in a 25-cc. casserole such a quantity of it as yields on ignition 1 g. of ash, add to it gradually 5 cc. of 9 n. $HClO_4$, and place the mixture on a steam-bath; when it has become hot, add cautiously 16 n. HNO_3, a few drops at a time, till 1 cc. has been added. Cover the casserole, and heat it on a steam-bath (*not over a flame*), adding gradually 1–3 cc. more 16 n. HNO_3, till nitrous fumes are no longer produced. Now heat the covered casserole on a wire-gauze over a small flame till the $HClO_4$ begins to fume strongly, reducing the heating if the action becomes too vigorous. (*Carry out this heating in such a way that, if an explosion should occur, personal injury can not result. See Note 6.*) Keep the mixture at fuming temperature as long as action is taking place. If charring has occurred, cool the mixture somewhat, add to it 1–2 cc. of 16 n. HNO_3 and 3 cc. of 9 n. $HClO_4$, and heat it at the fuming point as before. Repeat these operations till no charred material remains. Finally evaporate the mixture till the volume is reduced to 1–2 cc. Treat the resulting mixture (in place of the solid material) by P. 2.

Test fresh samples of the material for ammonium and for acidic constituents as described in A. A. Noyes' "Qualitative Analysis."

Notes.—1. It is important that the material to be analyzed be ground to a very fine powder or brought in some way into a form with a large surface; for otherwise much time will be lost in the later operations, and complete solution of the material may not be secured.

2. The quantity of the substance taken for analysis should always be approximately known; for a good qualitative analysis not only shows the presence or absence of the various elements in the substance, but enables their relative quantities to be estimated. Since 1 or 2 mg. of almost any element can be detected by this system of analysis, the presence of 0.1–0.2% of an element will be detected when one gram of a non-metallic material is taken, and this degree of delicacy is ordinarily sufficient. If much more than this quantity is taken, the precipitates may be so large that much time is consumed in filtering and washing them. Moreover, the

directions given for many of the separations are based on the assumption that there is present not more than 500 mg. of any one common element, nor more than 100–200 mg. of any one rare element. This is usually true when only 1 g. of material is used; but if it is likely to contain more than 50% of any one common element or more than 10–20% of any one rare element, the amount taken for analysis should be correspondingly diminished. Since alloys do not contain acidic constituents, it is directed to take only 0.5 g. of them for analysis.

3. When a complete analysis in the wet way is to be made, it is usually not worth while to make an extended preliminary examination in the dry way. The closed-tube test, however, must be made in order to determine whether organic matter is present. Its removal is essential since a dangerous explosion may occur in heating organic matter to fuming with perchloric acid (in P. 5), unless the material has previously been thoroughly treated with strong HNO_3. Moreover, certain organic substances, especially sugars and hydroxy-acids, such as tartaric, citric, and lactic acids, prevent the precipitation of the hydroxides of most of the elements; and they must therefore be removed in order to insure the precipitation of the tungsten and tantalum groups and of the elements which come down as hydroxides with ammonium acetate or hydroxide. Finally, a large quantity of organic matter of any kind interferes with the execution of the analysis; for example, with the operations of solution, filtration, and evaporation. Alloys do not contain organic matter or water; therefore the closed-tube test is not applied to them. When organic matter is found present, a rough quantitative determination of its amount is made by igniting a weighed portion in a porcelain crucible, so as to know how much of the material should be taken for the main analysis.

4. Blackening accompanied by a burnt odor or by the formation of a tarry deposit shows organic matter. Blackening alone does not show it; for salts of some of the metallic elements turn black on heating, owing to the formation of the black oxides. In a doubtful case 0.2 g. of the material may be heated with 2 cc. of 95% H_2SO_4, which causes charring or blackening when organic matter is present. Oxalates on heating blacken and emit a burnt odor to a much less extent than other organic substances and may not be detected by the closed-tube test, but they will be destroyed, wholly or in large part, by the subsequent fuming with $HClO_4$ (in P. 5).

5. Organic matter in the material to be analyzed might be destroyed by strong ignition; but this would result in complete volatilization of mercury and possibly of arsenic and other reducible elements, and in rendering some oxides very difficultly soluble. A wet process is therefore preferable. The process with $HClO_4$ and HNO_3, like the commonly employed one with H_2SO_4 and HNO_3, is of general applicability, being effective even with such stable substances as starch, cellulose, and paraffin. Most organic materials (thus paper, sawdust, tartrates) are largely decomposed by heating with the concentrated HNO_3 and $HClO_4$ on the steam-bath and yield a clear light-colored solution after the $HClO_4$ is brought to fuming for the first time; but some materials, for example paraffin, require that the operations be two or three times repeated. The $HClO_4$ process has the advantages over the H_2SO_4 process that barium, strontium, calcium, lead, and chromium are not converted into slightly soluble salts, requiring further treatment to bring them into solution; that less mercury is lost by volatilization; and that the oxides of the tungsten and tantalum groups are precipitated (in P. 6) more completely than when H_2SO_4 is present in the solution. In both processes germanium when present as chloride, and osmium (except when present as metal) are lost by vaporization. The loss of osmium is due to its conversion to the volatile tetroxide by the HNO_3 added. In the $HClO_4$ process ruthenium is also volatilized (unless it is present as the metal), since this acid has an oxidizing action strong enough to produce the volatile tetroxide of this element also.

6. In destroying organic matter with HNO_3 and $HClO_4$ the directions given in the Procedure must be carefully followed, especially in the respects that the material be first heated with the acids only on a steam-bath, not over a flame, and that fresh HNO_3 be added so long as any action takes place; for otherwise, there may result violent explosions by which the dish is blown to powder, especially with materials containing alcohols.

7. When the organic matter consists only of oil or fat, as in oil paints or pomades, it is best extracted with ether.

8. When the material is a solution, there may be lost in the evaporation prescribed in the second paragraph of the Procedure any volatile acid present in an acid solution, or ammonia present in alkaline solution; such substances should therefore be tested for in the original solution, rather than in the residue obtained on evaporation.

Procedure 2.—*Treatment of the Material with Hydrobromic Acid and Bromine.*—Place in a 50-cc. conical hard-glass ("pyrex") flask the weighed material in a very finely divided form (P. 1). Insert in the flask a two-hole cork stopper carrying a safety-tube extending to the bottom of the flask and a glass tube 60 cm. long and 0.8 cm. in bore, to serve as a reflux condenser. Connect the top of the condenser with a delivery-tube leading to the bottom of a test-tube containing just 5 cc. of saturated Br_2 solution. Pour gradually into the flask through the safety-tube 10 cc. of 9 n. HBr (see Note 4). Heat the mixture to boiling, and boil it gently for 10 minutes, rocking the flask, if necessary, to avoid bumping. If the Br_2 solution in the test-tube becomes decolorized, add to it from time to time 10 drops of liquid Br_2. Unless the material has all dissolved, cool the mixture to 50–60°, add from a dropper 0.5 cc. of liquid Br_2; and heat the mixture on a steam-bath for 10 minutes, adding more liquid Br_2 if its vapor above the mixture disappears. Reserve the solution into which the gas has been passed for use in P. 4. Note carefully whether there is an undissolved residue (even a slight turbidity or sediment) in the flask.

In case there is an undissolved residue, cool the mixture completely, and filter it with the aid of suction through a 5-cm. HF-washed hardened filter directly into a 50-cc. pyrex distilling flask whose side-arm has been extended by sealing on a glass tube (see figure 1 on next page); the flask being preferably provided with a glass stopper through which a safety-tube passes (as shown in figure 2; see Note 6). Remove the funnel from the flask; wash the residue on the filter first with 1–2 cc. of 9 n. HBr and then thoroughly with boiling water, rejecting the washings; and dry the filter. Treat the residue by P. 3; treat the HBr solution by P. 4, after uniting with it the residue from the HF and $HClO_4$ treatments of P. 3.

In case there is no undissolved residue, pour the HBr solution into a distilling flask, such as is described in the preceding paragraph; and treat it by P. 4.

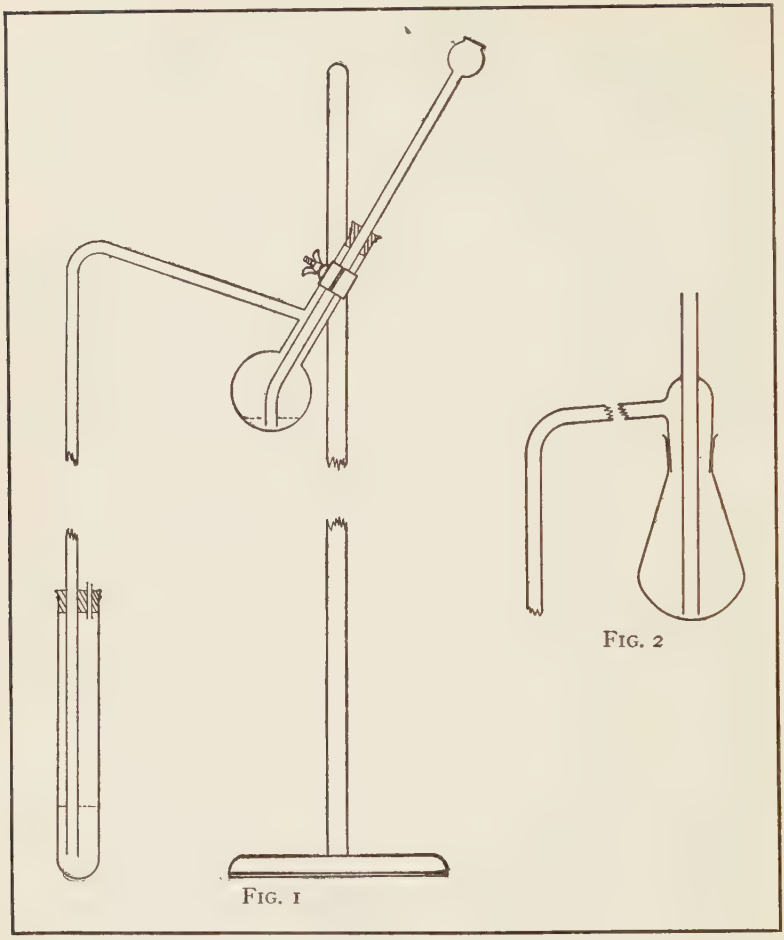

FIG. 2

FIG. 1

Notes.—1. By the treatment with hot concentrated HBr most substances are dissolved. There may remain unattacked, however, many metals, sulfides, and silicates, as well as a few oxides, sulfates, and phosphates. The addition of Br_2 serves to bring into solution nearly all the metals and sulfides that are not acted on by HBr alone.

2. The substance is first heated with HBr alone so that sulfides may, so far as possible, be dissolved and that the H_2S thereby liberated may escape from the flask before Br_2 is added; for otherwise it would be converted into H_2SO_4 and later cause the precipitation of lead, barium, and strontium sulfates. At the

same time H_2Se gas may be liberated from selenides, and pass off as a gas. A delivery-tube is therefore connected with the top of the condenser, and any gas evolved is led into Br_2 solution, which absorbs the H_2Se by converting it to H_2SeO_3. Little if any H_2Te gas is likely to pass over, since it reacts rapidly with oxygen, and since at most only a small proportion of a telluride is converted into H_2Te by the action of acids.

3. The HBr solution should be boiled, even though the material may have completely dissolved, in order to convert any liberated silicic acid into its insoluble form. When boiled for 10 minutes as directed, less than 1 mg. of SiO_2 remains in solution out of 500 mg. liberated from a decomposable silicate like sodium silicate; hence if there is no residue, it shows the absence of silicon in the substance.

4. If 9 n. HBr (s.g., 1.48–1.49) is not available, a suitable acid may be prepared in advance by boiling 15 cc. of 7.0–7.5 n. HBr (s.g., 1.40–1.42) down to 10 cc., since it is thereby concentrated to nearly 9 normal.

5. Even the elements which form bromides slightly soluble in water remain in solution wholly or largely in the concentrated HBr solution containing Br_2. Thus silver dissolves up to at least 100 mg., and lead up to 500 mg., owing to formation of complex anions; and thallium and mercury dissolve in large quantity, owing to the conversion of TlBr and HgBr by the Br_2 into $TlBr_3$ and $HgBr_2$.

6. It is very advantageous to use a pyrex distilling flask provided with a glass stopper through which a safety-tube passes; for in the subsequent distillations with HNO_3 and $HClO_4$, when osmium and ruthenium are distilled over, cork acts rapidly on the vapors of the tetroxides of these elements and prevents them from passing over completely into the distillate. Such a flask can readily be constructed by a glass blower. An especially convenient form is shown in figure 2. As this has the side-arm attached to the stopper, the successive operations of distilling and refluxing (in P. 5 and 6) can be carried out in it, thus avoiding transfer of the mixture to another flask.

Procedure 3.—*Treatment of the Undissolved Residue with Hydrofluoric and Perchloric Acids.*—Transfer the residue undissolved by HBr (P. 2) to a 25-cc. casserole; incinerate the filter in a platinum spiral, and let the ash fall into the casserole. Add 1–2 cc. of 16 n. HNO_3, and evaporate just to dryness.

Transfer the residue with the aid of a little water (see Note 8) to a small platinum dish (or crucible). Evaporate off the water, add 3–10 cc. of pure 27 n. HF (see Note 3), cover the dish with a piece of thin platinum foil, and digest the mixture on the steam-bath for about 15 minutes unless the residue dissolves more quickly. Remove the cover, add 3 cc. of 9 n. $HClO_4$ and 2 cc. of 16 n. HNO_3, and heat the mixture under a hood till white fumes of $HClO_4$ begin to be given off, taking care to avoid spattering (see Note 7 if a crucible is being used). Replace the cover loosely, and continue to heat for about 5 minutes at a temperature such that the $HClO_4$ fumes moderately, but does not rapidly evaporate. In case a clear solution has not resulted and the residue seems to be slowly dissolving, heat the mixture for 5–10 minutes longer, adding enough 9 n. $HClO_4$ to maintain the volume of liquid at about 2 cc. Finally evaporate the mixture carefully almost to dryness, and transfer the residue (see Note 8) with the aid of not more than 2–3 cc. of water to the distilling flask containing the HBr solution (P. 2).

Notes.—1. The residue is first treated with 16 n. HNO_3 in a casserole in order to destroy completely any bromide contained in it, which otherwise would set free Br_2 in the subsequent treatment and attack the platinum vessel. The HNO_3 also dissolves any metal reduced by the burning filter paper.

2. The digestion with HF decomposes nearly all silicates and dissolves SiO_2, forming H_2SiF_6. The strong HF causes in the cold the precipitation of the fluorides of calcium, lead, bismuth, thorium, and rare-earth elements, even when only 1 mg. is present in 5 cc. of solution; of lithium, magnesium, and strontium when more than 10 mg. are present; and of certain other elements when present in large quantity.

3. In using HF great care must be taken not to breathe its fumes nor to get it on the hands; for its vapor is extremely irritating, and the liquid produces dangerous burns. Solutions containing HF must not be allowed to come in contact with glass or porcelain. For holding and filtering HF solutions beakers and funnels of transparent "bakelite" may be used; and for measur-

ing out reagents graduates, pipettes, or droppers of this material are especially convenient; but platinum must be employed when solutions are to be heated over a flame.

4. By the evaporation of the HF solution with $HClO_4$ silicon is volatilized as SiF_4 and boron as BF_3, and the fluorides of other elements present in solution or as precipitates are transformed into perchlorates or oxides with volatilization of HF. The fluorides of calcium and the rare-earth elements are, however, only slowly attacked; and to ensure their solution the long heating with fuming $HClO_4$ is necessary; even then ThF_4 may not be completely dissolved.

5. The HF solution must not be evaporated to dryness before $HClO_4$ is added; for this would result in the volatilization of some titanium, tantalum, and columbium, in the form of TiF_4, TaF_5, and CbF_5.

6. The platinum dish is not attacked by fuming $HClO_4$, even in the presence of concentrated HNO_3. Even if AgBr is present, though some halogen is then liberated, the platinum is only slightly dissolved; thus when 100 mg. of AgBr are treated by P. 3, with the result that about one third of it dissolves, much less than 0.1 mg. of platinum passes into solution.

7. When a liquid is to be evaporated in a crucible, especially when it contains solid material, it is best to heat it within a larger iron crucible, which serves as an air-bath. The smaller crucible may be supported upon a circular disk of asbestos-board with a round hole cut out in the middle and slots cut out along the inner and outer edges.

8. When, as in these cases, a residue is to be transferred by using a minimum quantity of water, the water should be added 0.5 cc. at a time and the moist residue scraped out of the dish each time with a rubber-capped glass rod.

Procedure 4.—*Distillation with Hydrobromic Acid. Isolation of the Selenium Group.*—Set up in the way shown in figure 1 the distilling flask containing the HBr solution (P. 2 and 3). Insert the side-arm through a two-hole cork into the test-tube containing the 5 cc. of Br_2 solution into which the gas was passed in P. 2. Place the test-tube in a beaker of ice and water. Unless a glass-stoppered distilling flask is being used (see Note 6, P. 2), provide the flask with a clean cork stopper through which passes a long safety-tube reaching to the very

bottom of the flask. Distil the mixture over a small flame until about 3 cc. of solution remain in the flask, as shown by comparison with the volume of 3 cc. of water in a similar flask. Take care to condense all the distillate; also to keep the flask in motion, best by rocking it, so as to avoid bumping and overheating, especially towards the end of the heating (see Note 1).

Analyze the distillate for the selenium group by P. 21–25.

Treat the mixture in the distilling flask by P. 5*A* or 5*B*.

Notes.—1. The distillation must be made carefully, so that liquid may not be thrown over from the flask into the receiver. Inclining the apparatus, as shown in figure 1, helps to overcome this difficulty; but violent bumping must be avoided, which can best be done by rocking the stand supporting the flask. Care should also be taken that any substance which collects in the safety-tube or in the neck of the flask be carried down, by causing, through intermittent boiling, the liquid to flush out the safety-tube and to condense in the neck. In case even a minute portion of the HBr solution is thrown over during the distillation, the distillate, after all of it has been collected, should be re-distilled from a clean distilling flask, just as before, but into only 1–2 cc. of water; when only 2 cc. of liquid remain in the flask 2 cc. of fresh 9 n. HBr are poured into the flask, and the distillation is continued till only 2 cc. again remain. The residual liquid may be rejected if only a little was thrown over; otherwise it should be added to that left after the first distillation.

2. When the distillation is continued till the volume is reduced to 3 cc., all the selenium and nearly all the arsenic and germanium (thus, all of 500 mg. of arsenic except about 4 mg., and all of 25 mg. of germanium except 1.5 mg.) pass over into the distillate, in the form of $SeBr_4$, $GeBr_4$, and $AsBr_3$. Antimony and tin, when present in large amount, also distil over as $SbBr_3$ and $SnBr_4$ to the extent of a few milligrams; thus when 500 mg. are present 2–5 mg. of antimony and 8 mg. of tin may be found in the distillate. Mercury, whose bromide is somewhat volatile, does not distil over in appreciable amount; nor does any of the other elements do so. Osmium and ruthenium, though volatile when in the form of OsO_4 and RuO_4, remain completely in the residue, since they are reduced to lower valence states by hot HBr.

3. If, instead of stopping the evaporation of the HBr solution when the volume becomes 3 cc., the solution were evaporated al-

most to dryness (thus to 0.5 cc.), even in a boiling water-bath, by a rapid current of air, a large part of the tin (200 mg. out of 500 mg.) and a small part of the antimony (15 mg. out of 500 mg.) would be volatilized out of the solution. Under these conditions there is, however, no appreciable volatilization of mercury, osmium, or ruthenium.

4. The color of the HBr solution, after the volume has been decreased to 3 cc., often indicates the presence of certain elements. Thus the colors given in transmitted light by 5 mg. of the element to 3 cc. of 9 n. HBr are as follows: deep red by iron, rhodium, palladium, ruthenium, and osmium; orange-yellow to orange-red by platinum and gold; yellow by nickel; violet-red by copper; green or blue by vanadium and chromium; and violet by iridium. With 5 mg. of cobalt the color is pink when cold and blue when hot; with 100 mg., violet-red when cold and deep violet when hot.

5. The evaporation of the solution to a volume of 3 cc. may cause precipitation of AgBr or $BaBr_2$.

6. In the analysis of the distillate for the selenium group it is essential (in P. 22) that the acid concentration be between 4 and 6 normal. For this reason the volume of Br_2 solution in which the distillate is collected is restricted to 5 cc. (as directed in P. 2), 7 cc. of the 9 n. HBr are distilled over, and the receiver is kept cold so as to insure complete condensation of the acid.

Procedure 5.—*Distillation with Nitric and Perchloric Acids. Case A: Possible Presence of Osmium and Ruthenium.*—Cool the flask containing the residue from the HBr distillation (P. 4). Insert its side-arm into a graduated test-tube containing 10 cc. of 6 n. NaOH, surrounded with a mixture of ice and water. Add 4 cc. of 16 n. HNO_3 and 3 cc. of water; and distil the mixture slowly till brown Br_2 vapors are no longer seen in the delivery tube. Then add gradually to the distillate, kept ice-cold, Na_2O_2 powder, 0.5 cc. at first, then 0.2 cc. at a time till the mixture becomes colorless or till 1.0 cc. in all has been added. Continue to distil slowly till 4 cc. of liquid have passed over into the distillate, rocking the flask constantly to prevent bumping, and momentarily interrupting the boiling two or three times to cause the liquid to run out of the safety-tube. (Yellow to orange distillate, presence of OSMIUM.) If the distillate is colored, pour into the flask through the safety-

tube 2 cc. of water, and distil as before until 2 cc. more have passed over.

To the distillate, if it is colored, add 2 cc. of C_2H_5OH, and let the mixture stand 5 minutes. Filter out any precipitate that may separate. Into the solution pass H_2S gas slowly for 2 or 3 minutes. (Black precipitate, presence of OSMIUM.)

Place in the receiving test-tube 12 cc. of 6 n. NaOH, pour into the distilling flask 5 cc. of 9 n. $HClO_4$, and distil with the same precautions as before till about 3 cc. of liquid remain in the flask. If the distillate contains a red precipitate (indicating MERCURY), filter the mixture through an asbestos mat in a perforated crucible with the aid of suction. (Orange to dark-red distillate, presence of RUTHENIUM.) If the distillate is colored, pour into the flask through the safety-tube 2 cc. more 9 n. $HClO_4$, and distil again till 3 cc. of liquid remain, collecting the distillate in a fresh 6-cc. portion of 6 n. NaOH. If this second distillate is colored, unite it with the first one.

Treat the residual mixture in the distilling flask by P. 6.

To the distillate, if colored, add 2 cc. of C_2H_5OH, and let the mixture stand 5 minutes. (Black precipitate, presence of RUTHENIUM.)

Case B: Absence of Osmium and Ruthenium.—See Note 1. —Cool completely the flask containing the residue from the HBr distillation (P. 4). Pour into it 4 cc. of 16 n. HNO_3; and boil the mixture slowly till about half of the liquid has evaporated, rocking the flask constantly to prevent bumping. Pour into the distilling flask 5 cc. of 9 n. $HClO_4$, and distil, rocking the flask as before, till about 3 cc. of liquid remain (that is, till concentrated $HClO_4$ has been escaping for 1–2 minutes).

Treat the residual mixture in the distilling flask by P. 6.

Notes.—1. This Procedure has two purposes: first, the volatilization from the solution and the detection of the two elements osmium and ruthenium; and secondly, the conversion of the bromides produced by the HBr treatment into perchlorates or hydroxides and dehydration of the latter, in order that the tungsten and tantalum groups may be precipitated as completely as possible

in P. 6. The second, more important aspect of this Procedure will be fully discussed in the Notes to P. 6. It will suffice here to emphasize the fact that, to isolate these groups satisfactorily, the heating with the $HClO_4$ must be continued till the concentrated acid has been distilling out of the flask for 1–2 minutes. The following notes are confined to the volatilization and detection of osmium and ruthenium, and to the incidental volatilization of mercury.—Since the source and nature of the material usually shows whether the very rare elements osmium and ruthenium can be present, a much simpler alternative Procedure is given for the common case in which these elements do not need to be tested for.

2. Since the HBr solution can not be evaporated without the loss of much tin and some antimony (see Note 3, P. 4), the HBr is destroyed at once by heating the 3 cc. of solution with 16 n. HNO_3. The 4 cc. added suffice to decompose the HBr and provide for the oxidation and distillation of the osmium.

3. The osmium, which in the HBr solution exists in the quadrivalent state (as H_2OsBr_6), is oxidized by the boiling HNO_3 to the octivalent state, and vaporizes as the tetroxide OsO_4. The vapors are passed into 6 n. NaOH in order to absorb this volatile substance, which it does by converting it into $Na_2OsO_5 \cdot H_2O$.

4. The distillation with HNO_3, provided it is continued only till about half the acid has boiled off, causes all of the osmium, but none of the ruthenium, to pass over into the distillate. Thus with 1 mg. of osmium the whole quantity, and with 50 mg. all but 0.1–0.2 mg. distils over in the first operation, and with 50 mg. the remainder comes over on adding 2 cc. of water and distilling off 2 cc. of liquid; on the other hand, with 50 mg. of ruthenium under these conditions none whatever comes over. If, however, the distillation be continued so that the HNO_3 becomes concentrated, ruthenium begins to come over in small quantity. To avoid concentration of the acid, water is added, rather than more HNO_3, when the presence of osmium makes it desirable to repeat the distillation.

5. Even 0.2 mg. of osmium gives a perceptible yellow color to 10 cc. of NaOH solution; but the Br_2 produced by the decomposition of the HBr would also give it a yellow color and thus make it impossible to decide as to the presence or absence of a small quantity of osmium. To obviate this difficulty, some Na_2O_2 is added to the 6 n. NaOH; this, by converting the NaOBr and free Br_2 into NaBr with formation of O_2 gas, entirely destroys the bromine color; but it does not affect the color produced by the

osmium. Under these conditions absence of color shows absence of osmium, and the distillate need be tested no further. The Na_2O_2 is added to the NaOH after the Br_2 from the HBr has distilled over, rather than at the start, since much of the Na_2O_2 would then be lost by its spontaneous decomposition; and rather than at the end, in which case the distillate would become acid unless more NaOH were used.

6. If the distillate is colored, C_2H_5OH is first added to it so as to precipitate any ruthenium (see Note 8) that might possibly be present. This reduces the $Na_2OsO_5 \cdot H_2O$ to soluble sodium osmate, Na_2OsO_4, causing the solution to become colorless when little osmium is present, or light-red when much is present. The treatment of the solution with H_2S precipitates the osmium as sulfide. Mercury, which is the only other element that might have been volatilized in small quantity, does not give a precipitate with H_2S in NaOH solution.

7. After $HClO_4$ has been added to the liquid in the distilling flask and this acid has been concentrated to the fuming point, the ruthenium rapidly oxidizes to its tetroxide RuO_4, and this distils over; but, to carry it over into the distillate, the boiling is continued till some of the concentrated $HClO_4$ has distilled. If much ruthenium is present, in order to sweep it all out of the flask, a fresh portion of $HClO_4$ is added and the distillation is resumed. With 1 mg. of ruthenium all of it comes over during the first distillation; with 50 mg. all but about 1 mg. passes into the first distillate, and the remainder into the second distillate.

8. Even 0.2 mg. of ruthenium imparts a perceptible yellow color to 12 cc. of 6 n. NaOH: a colorless distillate therefore shows absence of ruthenium, and need not be further tested. By the NaOH the RuO_4 is probably converted into $Na_2RuO_5 \cdot H_2O$.

9. If the distillate is colored, C_2H_5OH is added to it, to confirm the presence of ruthenium. This produces a black precipitate of Ru_2O_{3-4}; less than 1 mg. giving at first a green color (due probably to $NaRuO_4$) and within five minutes a coagulated precipitate. Even 50 mg. of osmium give no precipitate.

10. Another element which may distil out of a boiling $HClO_4$ solution in appreciable quantity is mercury. The conditions under which it volatilizes have been well determined. It escapes from solutions only in the form of its halides, and then only when other halides are not present and when also the temperature of the solution is much above 120° (see also Note 3, P. 9). Hence it does not volatilize on evaporating the HBr solution in P. 4, nor upon boiling the HNO_3 solution in this Procedure. But since the

HNO_3 does not have much action on $HgBr_2$, a small part of the mercury present volatilizes when the $HClO_4$ begins to boil. The quantity so volatilized is not large (thus, 0.2 mg. with 5 mg. present or 20 mg. with 500 mg. present) provided the solution is distilled slowly; and it soon entirely ceases to come over, showing that the boiling concentrated $HClO_4$ rapidly converts the bromide into the perchlorate. When a large quantity of mercury is present, the $HgBr_2$ that volatilizes when the $HClO_4$ begins to boil mostly condenses as a white solid in the cold neck of the flask; and, if the boiling be slow, much of this washes back into the flask and is decomposed by the hot $HClO_4$. There is therefore no danger of losing enough mercury to affect its subsequent detection or quantity-estimation; but enough may distil over to produce a red precipitate of HgO in the NaOH solution. When such a precipitate forms, it is removed by filtration through asbestos; after which any color due to ruthenium becomes apparent, and the C_2H_5OH test for it can be satisfactorily applied. Paper can not be used for the filtration, since it rapidly reduces $Na_2RuO_5 \cdot H_2O$ to the black oxide or metal.

11. It is desirable to use in both the HNO_3 and the $HClO_4$ distillation a glass-stoppered flask, rather than a cork-stoppered one; for, as stated in Note 6, P. 2, cork rapidly reduces OsO_4 and RuO_4, and prevents complete volatilization of osmium and ruthenium.

Procedure 6.—*Precipitation of the Tungsten, Tantalum, and Gold Groups. Partial Removal of Alkali Elements.*—Cool the residual mixture from the distillations (P. 5), add to it gradually 10 cc. of 12 n. $HCHO_2$ (formic acid), and transfer the mixture to a 50-cc. conical pyrex flask (unless it is already in a flask like that shown in figure 2). Connect the flask with a small return-flow condenser, and boil the mixture gently for 15 minutes. (Residue in the hot solution, presence of the TUNGSTEN, TANTALUM, or GOLD GROUP, of SILVER, or UNATTACKED MATERIAL; no residue, absence of ANTIMONY, TIN, TUNGSTEN (except when phosphate is present), COLUMBIUM, TANTALUM, GOLD, MERCURY, PLATINUM, and PALLADIUM.) Filter the mixture while hot through a hardened HF-washed filter. Wash the filter with 2–4 cc. of boiling-hot water (or more if there is a crystalline residue that is rapidly

dissolving), adding these washings to the filtrate; then wash it thoroughly with hot water.

Treat the residue by P. 7.

Evaporate the filtrate to 10–12 cc., and cool the mixture under a water tap. (Crystalline precipitate, presence of much POTASSIUM, RUBIDIUM, or CESIUM.) Filter the cold solution through a small hardened filter with the aid of suction, and wash the precipitate thoroughly with the least possible quantity of ice-cold 3 n. $HClO_4$, not adding the washings to the filtrate.

Unite the precipitate with that obtained in P. 162, analyzing the mixture for potassium, rubidium, and cesium by P. 166–172.

Treat the filtrate by P. 61.

Notes.—1. The main purpose of Procedure 5 (as stated in Note 1, P. 5) is to displace the halogen acids from the bromides (and from any chlorides still present), and thus cause as complete a precipitation as possible of the tungsten and tantalum groups, especially of antimony, tin, tungsten, and molybdenum, and of tantalum, columbium, and titanium. This displacement is accomplished by a combination of the oxidizing action of concentrated HNO_3, the direct metathetical action of $HClO_4$ arising from its lesser volatility, and the strong oxidizing action which $HClO_4$ exerts when it becomes hot and concentrated.

2. The evaporations with HNO_3 and $HClO_4$ decompose completely all bromides, except solid AgBr (of which 200 mg. are only about one third decomposed). The bromides of tin and mercury, and in less degree that of antimony, are also only slowly decomposed; but the vigorous treatment prescribed suffices to destroy them completely. This is essential, since otherwise the oxides of tin and antimony will not be completely precipitated. This treatment also converts antimony to the quinquivalent state, and thus ensures its more complete precipitation with the tungsten and tantalum groups. To attain these results, however, the heating of the $HClO_4$ must be continued till about 2 cc. of the concentrated $HClO_4$ have distilled out of the flask. This strong heating serves also to dehydrate the hydroxides of the tungsten and tantalum groups, so that a more complete precipitation of these groups results.

3. Certain other changes may result from the strong oxidizing

action of the HNO_3 and fuming $HClO_4$. Thus manganous salts are partly oxidized to MnO_2, and a black precipitate of this substance may result when 100 mg. or more of manganese are present. Vanadyl salt, $VO(ClO_4)_2$, is converted to vanadic acid; and orange-yellow V_2O_5 may precipitate when much vanadium is present. Chromic salts are largely or completely oxidized to chromic acid. Gold bromide is almost completely decomposed into the metal with evolution of the halogen; and the bromides of palladium and platinum may be partly so decomposed when large quantities of these elements are present.

4. The fumed $HClO_4$ mixture is diluted and the mixture heated in order to cause more complete precipitation of the tungsten and tantalum groups. For this dilution pure water might be used so far as the separation of these oxides is concerned; but, in order at the same time to complete the precipitation of the gold group, to dissolve MnO_2 and V_2O_5, and to reduce trivalent thallium, 12 n. $HCHO_2$ is employed, and the mixture is boiled for 15 minutes. The behavior of the elements of the tungsten and tantalum groups and of some related elements is that shown by the following statements. The effects on these elements of diluting with water and of boiling with $HCHO_2$ are the same, except in the few instances noted.

The presence of even 1 mg. of columbium, tungsten, or tin, or of 1–2 mg. of tantalum or antimony, results in a noticeable residue, except in the combinations noted below. Moreover, large quantities of these elements when present alone are precipitated with this degree of completeness. When the dilution is made with $HCHO_2$, instead of water, less than 1 mg. of antimony remains in solution. After boiling with $HClO_4$ antimony is in the quinquivalent state, and the boiling with $HCHO_2$ does not reduce it to the trivalent state. These statements about the precipitation of antimony and tin are true, however, only when the halide has been all removed by thorough fuming with HNO_3 and $HClO_4$ as directed in P. 5; otherwise several milligrams may remain in solution.

The presence of phosphate (but not of vanadate) causes tungsten to dissolve readily, so that it may not be found in the tantalum group. Arsenate, if it has not been completely removed in P. 4, also causes tungsten to remain in solution.

Borate has little effect on the precipitation of the above named elements, except on that of tantalum in the special case that this element has been previously combined with the borate by fusion

or solution in a common solvent, when 10 mg. or more of tantalum may remain in solution. This case may be provided for, when borate is found present, by treating the mixture obtained at the end of P. 5 with HF (as is done in P. 3), whereby the excess of HF added volatilizes the boron as BF_3.

Sulfate in such amount as may be present in the original substance or formed from it by oxidation has little, if any, effect on the precipitation of the tungsten and tantalum groups.

Titanium, as explained in Note 5, remains in solution in small quantity; and this may cause a little tantalum also to dissolve; thus about 5 mg. of tantalum dissolve when 10–20 mg. of titanium are present and pass completely into solution. But when enough titanium is present to cause much of it to precipitate, the tantalum divides between the residue and solution; thus in an experiment with 50 mg. of titanium and 3 mg. of tantalum, in which (owing to mild fuming) 30 mg. of titanium remained in solution, 1 mg. of tantalum was found in the residue. Since under the conditions of P. 5 and 6 only about 4 mg. of titanium dissolve, the tantalum in solution should not exceed 2–3 mg., and it will be less than this when enough titanium is present to give a precipitate. Hence, in almost all cases the solvent action of titanium is negligible. Titanium does not have a corresponding solvent effect on columbium, a precipitate being always obtained even with 1 mg. of columbium.

5. The residue undissolved by the hot diluted $HClO_4$ solution contains, in addition to the elements (antimony, tin, tungsten, tantalum, and columbium) named in Note 4 which except in a few combinations can be regarded as completely precipitated, nearly all the molybdenum and titanium when more than a small quantity of these elements is present (except that molybdenum, like tungsten, may be wholly dissolved when phosphate or arsenate is present). Thus, when present alone, there will be found in the residue any molybdenum in excess of about 3 mg. when water is used, or of 1.5–2.0 mg. when $HCHO_2$ is used; also any titanium in excess of about 4 mg. when either water or $HCHO_2$ is used. Even 20 mg. of titanium may, however, dissolve, if the $HClO_4$ is heated less strongly (thus by fuming it for a short time in an open dish, instead of boiling off the acid in a flask). Titanium, when present with more than an equivalent quantity of phosphate, is precipitated much more completely. When present with much zirconium, on the other hand, a much larger quantity of titanium passes into solution; thus a clear solution results

when a mixture of 75 mg. of titanium and 100 mg. of zirconium is subjected to the $HClO_4$ treatment and diluted.

6. Besides the seven elements of the tungsten and tantalum groups, considered in Notes 4 and 5, there are five others, namely, zirconium, thorium, tellurium, vanadium, and bismuth, which when present alone pass wholly into the hot $HClO_4$ solution, but in certain combinations are carried out completely or almost completely into the residue, as shown by the following statements.

All but a few milligrams of zirconium or of thorium is precipitated when more than an equivalent quantity of phosphate is present with it.

Nearly all the tellurium (95 mg. out of 100 mg., and all of 5 mg.) is carried out when much tin (300 mg.) is present; but scarcely any lead (less than 0.5 mg. out of 5 mg.) is carried down with tin.

Bismuth (up to 200 mg.) may be carried out completely with a large quantity (400 mg.) of antimony.

Phosphorus is precipitated with tin as stannic phosphate; and arsenic (if it had not been removed by the HBr distillation) would also be precipitated with tin as stannic arsenate.

Vanadium may be precipitated largely or even completely as yellow stannic vanadate when much tin is present, in case the fumed $HClO_4$ mixture is diluted with hot water; thus with 500 mg. of tin all of 10 mg. of vanadium and 70–85 mg. out of 100 mg. of vanadium are carried down. When the $HCHO_2$ treatment is used, the orange-yellow stannic vanadate precipitate becomes greyish-white, and more of the vanadium goes into solution as the blue vanadyl salt, but some of it is retained by the precipitate; thus with 500 mg. of tin, 8 mg. out of 80 mg. of vanadium, and 4 mg. out of 5 mg., are carried down.

Vanadium, when present alone in sufficient quantity to be precipitated as V_2O_5 by the $HClO_4$ fuming, remains partially undissolved when water is used; but it is all brought into solution by the $HCHO_2$ treatment as the blue vanadyl salt, except in case as much as 100 mg. of vanadium are present, when 15–20 mg. may remain as a residue.

The detection of all these elements, which are doubtless also carried out in other combinations not specially investigated, is therefore provided for both in the $HClO_4$ solution and in the residue from it. Various other elements may also be carried down in small quantities with the oxides of the tungsten and tantalum groups.

7. If water were used for the dilution of the fumed $HClO_4$ mixture, the residue would contain Au, Pd, Pt, AgBr, MnO_2, V_2O_5, and $PbCrO_4$, when the corresponding elements are present in large quantity; but a large proportion of each of these elements (except of gold, of which little if any remains unprecipitated) would be found also in the filtrate. When, however, $HCHO_2$ is employed and the mixture is boiled, as directed in the Procedure, all the manganese and chromium pass into the filtrate; also all or nearly all the vanadium unless it is present with elements of the tungsten and tantalum groups. Moreover, all the gold, palladium, platinum, and mercury are precipitated (as dark-orange Au, black Pd or Pt, or liquid Hg). A small proportion of any rhodium and of any iridium, and a large part (perhaps 50%) of any silver present in the solution may also be precipitated as metals. Other reducible elements, such as copper, bismuth, and tellurium, are not precipitated by this treatment. This is also true of selenium, which however has been previously removed in P. 4.

8. The boiling with $HCHO_2$ also serves to reduce certain elements in the solution to a lower state of oxidation. Thus thallium, chromium, manganese, and vanadium will be present in the filtrate as thallous, chromic, manganous, and vanadyl salts, and iron mainly as ferrous salt. This makes possible the immediate removal of thallium (as TlBr in P. 61), and diminishes the extent to which the H_2S is decomposed (with deposition of sulfur) in the subsequent treatment with that reagent.

9. The quantity of iridium and rhodium precipitated seems to depend mainly on contact catalytic effects. Thus $HCHO_2$ solutions containing a small quantity (10 mg.) of only these elements yield on boiling little, if any, precipitate. This sometimes happens, at any rate with iridium, even when the solution contains 100 mg.; but at other times, apparently when the precipitation accidentally gets started, as much as 10 mg. of iridium or 20 mg. of rhodium, out of 100 mg., is precipitated. Moreover, even small quantities (5 mg.) of these elements may be four-fifths precipitated when platinum (and presumably other precipitated elements) are present in considerable quantity. The precipitation of iridium does not depend on whether it has been previously reduced to the trivalent state.

10. In order that mercury may be completely precipitated, it is essential that the $HClO_4$ mixture be strongly fumed (as directed) so as to destroy all the halide, that the $HCHO_2$ used be as strong

as 12 n., and that the mixture be boiled (not merely heated on a steam-bath) for at least 15 minutes. The concentration of the $HClO_4$ has, however, little influence. Longer boiling is undesirable when platinum elements may be present, since it precipitates a larger proportion of rhodium and iridium. Thallium is completely reduced to thallous salt by boiling 15 minutes even with 6 n. $HCHO_2$.

11. It follows from the foregoing considerations, if no residue remains after the boiling with $HCHO_2$, that antimony, tin, tungsten (except when phosphate is present), columbium, tantalum, gold, mercury, platinum, and palladium are not present in the material in quantity exceeding 1–2 mg.; also that molybdenum is not present in quantity exceeding 2–3 mg. (except when phosphate is present), nor titanium in quantity exceeding 4 mg. (except when zirconium is also present). It should be borne in mind, however, that this limiting quantity may cause only a turbidity in the case of an oxide of the tungsten and tantalum groups, and may give rise only to a darkening of the liquid in the case of platinum or palladium (or of much rhodium or iridium), or to a black scum or minute droplets of metal in the case of mercury, or to a red coloring of the solution at the beginning of the $HCHO_2$ treatment in the case of gold. Time should therefore be allowed for a sediment to form before deciding that the elements are absent.

12. When more than 300 mg. of potassium are present, a crystalline precipitate of $KClO_4$ forms even in the hot $HClO_4$ solution; but the washing with hot water dissolves this. After cooling the solution a precipitate of $KClO_4$, $RbClO_4$, or $CsClO_4$ separates when only 30–50 mg. of the alkali elements are present. It is desirable to remove from the main solution any large quantity of these alkali perchlorates that may be present. Otherwise they may separate with the alkaline-earth group when this is precipitated (in P. 151) by adding $(NH_4)_2CO_3$ and C_2H_5OH to the solution evaporated to a small volume. The precipitate is washed with a minimum quantity of ice-cold 3 n. $HClO_4$, so as to wash away very little of it before it is tested for the alkali elements. Other perchlorates will not separate upon cooling, since they are readily soluble. Any small precipitate (such as a little $CaSO_4$) may be rejected.

Procedure 7.—*Extraction of the Tungsten and Tantalum Groups from the Residue Undissolved by Perchloric Acid.*—Transfer the residue from the $HCHO_2$ treatment (P. 6) to a platinum dish or bakelite beaker (see Note 1). Pour over it 5–10 cc. of 27 n. HF; and heat the mixture on a steam-bath for 3–10 minutes. Cool the mixture, dilute it with 2½ times its volume of cold water, filter it through a hardened filter supported in a bakelite or hard-rubber funnel, and collect the filtrate in a platinum dish. Wash the residue thoroughly.

Treat the residue by P. 8.

Analyze the filtrate for the tungsten and tantalum groups by P. 30–49.

Notes.—1. When a precipitate is to be transferred from a filter, it is advisable in general to proceed as follows. Open the filter, tear off the part of it to which no precipitate adheres, and spread the remainder along the side of the dish; pour the solvent over the paper and rock the dish to and fro, at the same time rubbing the precipitate off the filter with a glass rod. Draw the filter out of the solution, press the liquid out of the paper with the rod, and throw away the paper. When it is important to avoid introducing paper-pulp into the liquid, or when it is difficult to dissolve or wash the precipitate off the paper, it is well to employ a hardened filter for the previous filtration; this also enables suction to be used in case it prove desirable.

2. As to the handling of HF solutions, see Note 3, P. 3. As to the precipitation of various elements by HF, see Note 2, P. 3.

3. In the concentrated HF all the oxides of the tungsten and tantalum groups dissolve, except that of tin when this is present in large quantity; but this also dissolves on the addition of cold water. Of the other five elements, referred to in Note 6, P. 6, as being carried down with the tungsten and tantalum groups, zirconium, tellurium, and vanadium are also completely dissolved by the HF treatment; but bismuth dissolves only to the extent of 2–5 mg., and thorium scarcely at all.

4. In case $CaSO_4$, $SrSO_4$, $PbSO_4$, Bi_2O_3, or $Th_3(PO_4)_4$ is present in the residue from the $HClO_4$ solution, these compounds are converted into the corresponding fluorides (that of thorium perhaps only partially). No calcium or thorium dissolves; but 10–15 mg. of lead and 2–5 mg. of bismuth may pass into the HF solution. Lead need not, however, be tested for in the analysis

of the tungsten and tantalum groups; for some $PbSO_4$ (corresponding to 15–20 mg. of lead) always passes into the $HClO_4$ solution in P. 6; and, when a large amount was originally present, most of the lead remains undissolved by the HF and passes into solution in P. 8.

Procedure 8.—*Treatment of the Undissolved Residue with Sodium Carbonate Solution.*—To the residue undissolved by HF (P. 7) in a 150-cc. conical flask add 50 cc. of 3 n. Na_2CO_3, heat the mixture to boiling, and add 10 g. of solid Na_2CO_3. Insert a rubber stopper carrying a glass tube 60 cm. long and 0.8 cm. in bore, to act as a reflux condenser. Boil the mixture gently for 15 minutes. Filter the hot mixture through a hardened filter, and wash the residue thoroughly with hot water. Reject the filtrate and washings. Pour repeatedly through the filter a hot 10-cc. portion of 3 n. $HClO_4$; and wash the residue.

Treat the residue by P. 9.

Analyze the $HClO_4$ solution by P. 70–158, uniting the group precipitates with those obtained from the main $HClO_4$ solution resulting from P. 6.

Notes.—1. The residue from the HF treatment may contain, in addition to unattacked material, PbF_2, CaF_2, SrF_2, BiF_3, ThF_4, and AgBr. By the boiling with concentrated Na_2CO_3, all these fluorides, except ThF_4 and some CaF_2 (when much is present), are converted into carbonates. These carbonates subsequently dissolve on treatment with $HClO_4$; and the resulting solution is tested for the elements that may be present by subjecting it to the general scheme of analysis, beginning with the H_2S precipitation. The solution is not united with the main $HClO_4$ solution, since it may contain sodium coming from the Na_2CO_3; but the group precipitates may be united with the corresponding ones from the main solution.

2. $BaSO_4$, if originally present, will be found in the HF residue. It is converted into carbonate by the boiling Na_2CO_3 solution; but the conversion may not be quite complete when a large quantity is present; thus 1 g. of $BaSO_4$ treated by this Procedure left a residue of 5–10 mg. Anhydrous $Cr_2(SO_4)_3$ will also be left largely (as a pink or gray powder) in the HF residue; but it is changed only very slowly (into hydroxide) by the Na_2CO_3 treatment. Thus when a sample containing 100 mg. of

chromium was treated by P. 2–8 (omitting the HF treatments in P. 3 and 7), it dissolved slowly in the 9 n. HBr in P. 2, about three-fourths of it remained as residue in P. 6, and only 6 mg. of chromium passed into solution in P. 8.

3. The mixture is boiled with a reflux condenser, rather than in an open vessel, so as to avoid the danger of volatilizing with the steam a small quantity of metallic Hg.

Procedure 9.—*Extraction of the Gold Group and of Silver from the Residue from the Sodium Carbonate Treatment.*—Transfer the residue undissolved by $HClO_4$ after the Na_2CO_3 boiling (P. 8) to a casserole. Pour over it 3–9 cc. of 16 n. HNO_3 and 1–3 cc. of 12 n. HCl, and heat the mixture on a steam-bath for 10 minutes unless the residue has previously dissolved. Evaporate the mixture to a volume of 0.5–1.0 cc., taking care not to overheat the residue. Add 12 cc. of water, heat the mixture to boiling, and filter it through a HF-washed filter. Wash the residue.

Analyze the filtrate for the gold group by P. 51–57.

Through the filter containing the residue pour repeatedly a warm 10-cc. portion of 15 n. NH_4OH (or if the residue is large, digest it in a casserole with this reagent, and filter the mixture). Boil the solution till most of the NH_3 is expelled, add a drop of 6 n. HCl, and acidify it with $HC_2H_3O_2$. (White precipitate, presence of SILVER.) If silver is found present, wash the undissolved residue with 6 n. NH_4OH till it is free from silver. Dry the filter and residue thoroughly.

Treat the residue, in case it is non-metallic, by P. 10; in case it is metallic, by P. 11.

Notes.—1. By the treatment with HNO_3 and HCl the gold-group metals, Hg, Au, Pt, Pd, are all dissolved with formation of soluble complex halogen acids (such as H_2HgCl_4, $HAuCl_4$, H_2PdCl_4, H_2PtCl_6); and the AgBr and Ag are converted into solid AgCl. Any rhodium or iridium present, owing to its having been precipitated by the boiling with $HCHO_2$, commonly dissolves partially, but not completely; so that both the solution and residue are later tested for these elements. Concentrated acids are employed and the mixture is heated for 10 minutes, so as to dissolve as much of these elements as possible.

2. An acid mixture is used containing much more HNO_3 than HCl and the mixture is evaporated to a small volume, so that nearly all the chloride in excess of that combined with the gold-group elements may be destroyed; for much chloride interferes with the subsequent analysis of the gold group.

3. The acid mixture is evaporated only to 0.5–1.0 cc., not to complete dryness, so that $HgCl_2$ may not volatilize; for a small quantity of it is largely lost when a HNO_3 solution (though not when a HCl solution) is evaporated to dryness, even on a steam-bath, since there is then no excess of HCl to convert it into the complex acid H_2HgCl_4. (See also Note 10, P. 5.)

4. Since a large part of any silver present in the material may be found here (because AgBr is only slowly decomposed by the boiling $HClO_4$ in P. 5), the residue is tested for silver. 200 mg. or more of silver as AgCl, in the disintegrated form produced by boiling AgBr with HCl and HNO_3, dissolve quickly in hot NH_4OH.

Tabular Outline II A

TREATMENT OF NON-METALLIC MATERIAL UNATTACKED BY ACIDS

Residue (from P. 9):

Oxides of Al, Cr, Ti, Zr, Sn.	Sulfates of Cr, Ba.
Phosphates of Ti, Zr, Th, Ce. . .	Fluorides of Th, Ca.
Silicates of various elements.	Metallic Ir, Rh, C.

Fuse with $K_2S_2O_7$, add cold water, and filter. Heat the residue with HCl, filter. Unite the two filtrates (P. 10).

Residue:
Pb, Ba, Sr, Ca, Cr, as sulfates.
Si, W, Ta, Cb, as oxides.
Ir as metal.
Unattacked silicate or SnO_2.
Treat with HF (P. 7).

Residue:
Ba, Cr, as sulfates.
Pb, Sr, Ca, as fluorides.
Silicate. SnO_2.
Ir as metal.
Boil with Na_2CO_3 (P. 8).

Solution: Si, W, Ta, Cb, as complex fluorides. *Treat by P. 30–48.*

Filtrate. *Reject.*

Precipitate:
Pb, Ba, Sr, Ca, as carbonates.
Cr as hydroxide and sulfate.
Silicate. SnO_2.
Ir as metal.
Add $HClO_4$ (P. 8).

Solution: Pb, Ba, Sr, Ca. *Test by P. 71, 81, 82; 151–7.*

Residue: $Cr_2(SO_4)_3$. Silicate. SnO_2. Ir. *Fuse with Na_2O_2 (P. 11).*

Filtrates. *Adjust hydrogen-ion concentration, saturate with H_2S (P. 70–71).*

Precipitate:
Se, As, Sb, Sn.
Tellurium group.
Copper group.
Distil with HBr (P. 2, 4).

Filtrate: Later groups, also Tl. *Analyze by P. 90–158.*

Distillate. Se, As. *Test by P. 21–24.*

Residue:
Evaporate with HNO_3 and $HClO_4$, boil with 12 n. $HCHO_2$ (P. 5–6).

Residue: Sb, Sn as oxides. *Dissolve in HCl, test by P. 33–34.*

Filtrate. *Treat with H_2S (P. 70–71).*

Precipitate: tellurium–copper groups (*P. 70–79; 81–86*).

Procedures and Notes

Procedure 10.—*Fusion of Unattacked Material with Potassium Bisulfate.*—Transfer the residue undissolved by HCl and HNO_3 (P. 9), if it is non-metallic, to a watch-glass or crucible cover, incinerating the filter paper. Add this residue gradually to a fused-silica ("vitreosil") crucible containing 10 g. of $K_2S_2O_7$ in a state of fusion. Cover the crucible, heat it so that its lower part is dull red and SO_3 fumes escape only

slowly when the crucible is uncovered, and keep it at this temperature for 20 minutes. Let the crucible cool; then loosen the melt with a spatula or knife, transfer it to a small porcelain mortar, and crush it to a powder. Transfer this to a casserole, add 25 cc. of cold water, and let the mixture stand till the solid is disintegrated. Filter the mixture through a hardened filter. Transfer the residue to a casserole, and heat it with 5–10 cc. of 12 n. HCl in a covered casserole on a steam-bath as long as the residue is dissolving; evaporate the mixture to 1 cc., add 5 cc. of water, filter, and wash the residue. Unite this filtrate with the aqueous extract; and treat the united solutions by the third, fourth, and fifth paragraphs of this Procedure.

Treat with HF by P. 7 the residue from the HCl digestion, and treat by P. 8 any residue remaining after this treatment. Test the HF solution obtained in P. 7 for tungsten, tantalum, and columbium by P. 30–48. Test the $HClO_4$ solution obtained in P. 8 for lead by P. 71, 81, and 82, and for barium, strontium, and calcium by P. 151–157. Dry any residue left after P. 8, and fuse it with Na_2O_2 by P. 11.

Adjust the hydrogen-ion content of the united solutions by P. 70, and dilute to 100 cc. Pass into the cold mixture a slow current of H_2S for 15 minutes. Filter, and wash this H_2S precipitate.

Analyze the filtrate from the H_2S precipitate for the aluminum, nickel, zirconium, rare-earth, and alkaline-earth groups by P. 90–158; also testing for thallium by Note 5, P. 94.

Treat the H_2S precipitate (as if it were an original material) with HBr by P. 2 followed by P. 4, testing the distillate for selenium and arsenic by P. 21–24; evaporate the residual liquid with HNO_3 and $HClO_4$ (P. 5 *B*), not collecting the distillates; and boil the mixture with $HCHO_2$ and filter (P. 6). (See, however, Note 7.)—Treat the $HClO_4$-$HCHO_2$ solution obtained in P. 6 by P. 70–79 and P. 81–86, to detect tellurium-group and copper-group elements.—Dissolve the residue obtained in P. 6 in just 10 cc. of 12 n. HCl, and test the solution for antimony and tin by P. 33 and 34.

Notes.—1. For the substances likely to be present in the residue subjected to the fusion and for a survey of the process covered by this Procedure, see Tabular Outline II A.

2. The fusion with the strongly acid flux $K_2S_2O_7$ (potassium bisulfate or pyrosulfate) converts into sulfates the oxides of aluminum, chromium (even in chromite, $FeOCr_2O_3$), titanium, and zirconium, and any thorium or rare-earth phosphate or fluoride, which may have resisted the previous treatments. Finely divided metallic Rh (see Note 1, P. 9), but not Ir, is slowly converted into its sulfate by the fusion. Native or ignited SnO_2 is only slowly attacked by $K_2S_2O_7$; and, if much of it was present in the original material, a large proportion (50–60%) may still be unattacked. A few other substances also may be only partially decomposed; for example, certain silicates and anhydrous $Cr_2(SO_4)_3$.

3. The elements named in Note 2 pass for the most part into the water extract, provided care has been taken not to expel too much of the SO_3 by overheating. The mixture is kept cold to avoid the precipitation of $Ti(OH)_4$ through hydrolysis.

4. Yet, after extracting the melt with water, even though the material has been decomposed by the flux, there may remain a precipitate of anhydrous sulfates, or of oxide or phosphate of tin or titanium, or of a phosphate or double sulfate of thorium or rare-earth elements. The digestion with hydrochloric acid serves to dissolve these substances.

5. Any residue undissolved by the digestion with hydrochloric acid may consist of, *a*, precipitated SiO_2, WO_3, Ta_2O_5, or Cb_2O_5; *b*, $PbSO_4$, $CaSO_4$, $SrSO_4$, $BaSO_4$; *c*, metallic Ir; *d*, incompletely attacked SnO_2, $Cr_2(SO_4)_3$, or silicates. The residue is treated first with HF as in P. 7 to dissolve the substances designated *a*; and then with Na_2CO_3 and $HClO_4$, as in P. 8, to dissolve those designated *b*. Any residue that still remains, consisting of substances *c* and *d*, is fused with Na_2O_2, as described in P. 11.

6. The solution obtained by uniting the aqueous and acid extracts from the $K_2S_2O_7$ fusion is saturated with H_2S, after adjusting the acid content, so as to separate the precipitable elements from the large quantity of potassium salts, and thus make it possible to submit these elements to the HBr distillation and the $HClO_4$ fuming in P. 2, 4, and 5. Since the quantity of SO_3 retained by the $K_2S_2O_7$ after the fusion is somewhat indefinite, it is advisable to adjust the hydrogen-ion concentration as in P. 70 with the aid of the indicator methyl violet; but, when

the color of the solution makes this impracticable, it may be assumed that the $K_2S_2O_7$ retains nearly the amount of acid appropriate for the H_2S precipitation, and that therefore there should be added only enough NH_4OH to neutralize the 1 cc. of HCl left after evaporating the solution of the residue in this acid. The solution is not heated during the H_2S precipitation (as is ordinarily done in P. 71), since this might cause precipitation of hydroxides and basic phosphates of quadrivalent and rare-earth elements.

7. In the last paragraph of the Procedure provision is made for the isolation of the selenium group by dissolving the H_2S precipitate in HBr and Br_2 and distilling. When the elements of this group need not be tested for in the solution from the $K_2S_2O_7$ fusion, the process can be somewhat shortened by dissolving the H_2S precipitate in 3–10 cc. of 12 n. HCl, with addition of a little HNO_3 if necessary; then evaporating to 1–2 cc., adding twice the volume of 16 n. HNO_3 and 5 cc. of 9 n. $HClO_4$, and boiling the liquid down in a flask till only 3 cc. of $HClO_4$ remain, so as to destroy chlorides and cause the precipitation of antimony and tin oxides; then diluting with 10 cc. of water, boiling, and filtering; and finally treating the solution and residue resulting therefrom as described in the last two sentences of this Procedure.

8. A vitreosil crucible is recommended for the fusion, since it is not attacked by $K_2S_2O_7$ and no foreign elements are introduced into the analysis. If such a crucible is not available, a platinum crucible may be used; but in that case a little platinum (0.5–1.0 mg.) will pass into the solution, which it is well to remove by shaking with precipitated silver the mixture obtained by uniting the aqueous extract of the fusion and the HCl solution of the residue. To ensure the easy removal of the melt from a platinum crucible, cool it suddenly by plunging its lower half into water in a large casserole and keeping it there till the melt is cold. This treatment is usually unnecessary with a vitreosil crucible, because on cooling it contracts less than the melt.

Procedure 11.—*Fusion of Unattacked Material with Sodium Peroxide.*—Treat the unattacked material from the acid treatment (P. 9) if it is metallic, and treat any residue from the $K_2S_2O_7$ fusion (P. 10), as follows. Incinerate the filter, and transfer the residue and ash, gradually if violent action occurs, to a nickel crucible in which (according to the size of

the residue) 3–5 g. of Na_2O_2 have been brought to a state of fusion by heating the lower part of the crucible to dull redness. Continue the heating 3–20 minutes, but only till the residue has dissolved, maintaining a temperature sufficient to keep the mass fluid.

Let the crucible cool, place it on its side in a covered casserole, and add 30 cc. of cold water. After violent effervescence has ceased, rinse out the crucible with not more than 5 cc. of water, and remove it. Heat the covered casserole on a steam-bath for 10 minutes. Pour the solution into a 200-cc. conical flask, neutralize it by adding 12 n. HCl, at first 1 cc. at a time and towards the end a few drops at a time, constantly cooling the mixture under a tap. Then add 1 cc. of C_2H_5OH and just 2.5 cc more of 12 n. HCl, cover the flask, and heat it on a steam-bath as long as the residue is dissolving. (If there is still a residue, filter it out, digest it for 5–10 minutes on a steam-bath with 5 cc. of 12 n. HCl and 1 cc. of 16 n. HNO_3, evaporate the mixture just to dryness, add a little water and a few drops of HCl, and unite the mixture, without filtering it, with the main solution.)

Cool the mixture, pour it into a 100-cc. pyrex bottle, and saturate it with H_2S. Insert a rubber stopper, fasten it securely by wiring it in or clamping the bottle in a pressure-bottle frame, immerse the bottle in a vessel of water, and boil the water gently for about an hour. Let the bottle cool, and open it. (If the mixture does not smell strongly of H_2S, resaturate it, close the bottle, and heat it again in boiling water for 30 minutes.) Add 50 cc. of water, and saturate the cold mixture with H_2S. Filter it through a hardened filter, and wash the precipitate with hot water.

Analyze the filtrate by P. 91–149 for the aluminum, nickel, zirconium, and rare-earth groups.

Transfer the H_2S precipitate to a conical flask, and treat it (as if it were an original material) with HBr by P. 2, not filtering out any residue, and then by P. 4. Analyze the distillate for the selenium group by P. 21–25. Treat the residual liquid

(P. 4) with HNO_3 and $HClO_4$ by P. 5*A*, testing the distillates for osmium and ruthenium. Treat the residual liquid (P. 5) with $HCHO_2$ by P. 6.—Analyze the filtrate obtained in P. 6 for silver by P. 61–62, and for the tellurium and copper groups by P. 70–86.—Treat the residue obtained in P. 6 by P. 7, followed by P. 9; and analyze the HF solution (P. 7) for the tungsten and tantalum groups by P. 30–49, and the HCl-HNO_3 solution (P. 9) for the gold group by P. 51–57. (If there is a residue, of Rh or Ir, at the end of P. 9, dry it, and treat it by P. 11, uniting any resulting H_2S precipitate with the main one obtained in P. 71, and rejecting the filtrate.)

Notes.—1. Of the metallic substances possibly present in a residue undissolved by acids (see Tabular Outline II), all are energetically acted upon by this strongly oxidizing flux, except the platinum metals and their alloys; and even 500 mg. of these are completely dissolved in less than 20 minutes fusion, provided they have been finely powdered, as directed in P. 1. This flux also renders soluble any stannic oxide or silicates which have not been acted upon by $K_2S_2O_7$.

2. By the fusion the platinum metals are converted into oxides or sodium salts. Osmium and ruthenium yield the osmate Na_2OsO_4 and ruthenate Na_2RuO_4, which dissolve in water forming orange-yellow and orange-red solutions, respectively. Rhodium, iridium, platinum, and palladium form oxides or sodium salts nearly insoluble in the alkaline medium; thus not more than 2–3 mg. of palladium and less than 1 mg. of iridium or platinum pass into solution. The platinum compound yields after the acidification a dense yellow powder, $Pt_2O_3 \cdot 2H_2O$, which dissolves only slowly in hot 12 n. HCl or even in HCl and HNO_3. Of the other elements coming from resistant alloys or silicates, those that form acids in their higher valence states, such as silicon, aluminum, beryllium, tungsten, molybdenum, chromium, pass into the aqueous solution of the melt, and those that do not form acids, such as iron, nickel, cobalt, separate as oxides when the melt is treated with water. Tin and titanium may divide between the aqueous extract and residue from it.

3. Platinum and silver crucibles are so much attacked that they can not be employed. As the nickel is much acted upon by the flux and much nickel is thereby introduced into the analysis, the fusion should be discontinued as soon as the residue has all

dissolved in the melt. The nickel separates, on the addition of water, as a fine black precipitate consisting of $Ni_3O_4 \cdot 2H_2O$, which quickly dissolves when the solution is acidified. To determine the nature and quantity of other impurities introduced from the crucible and flux, a blank fusion and analysis of the melt should be made.

4. After dissolving the melt, the mixture is heated on a steam-bath to destroy the excess of Na_2O_2, which would otherwise decompose the H_2S subsequently passed in. There is no volatilization of osmium or ruthenium in this heating, since these elements are present as Na_2OsO_4 and Na_2RuO_4. But upon acidification some of the volatile OsO_4 may be formed. During the neutralization, therefore, the mixture is kept cold to avoid loss of osmium; and, before heating the acidified solution, C_2H_5OH is added to it to reduce the osmium to a lower valence state. Ruthenium does not volatilize after acidification, even when no C_2H_5OH is added.

5. When there is a residue after heating the acidified solution, it is subjected to a more powerful solvent action by filtering it out and heating it with strong HCl and HNO_3. This dissolves any metallic Ni or Ni_3O_4, and most other basic oxides. Since it may not dissolve all the Pt_2O_3 or any precipitated AgCl, and since acidic hydroxides insoluble in acids, such as H_2SiO_3 or H_2WO_4, may have precipitated on acidifying the solution of the melt, any residue still remaining is not filtered out, but is allowed to become included in the H_2S precipitate. Thereby any Pt_2O_3 or AgCl present is converted into the corresponding sulfide.

6. The whole mixture is treated with H_2S to separate from the large quantity of sodium salt and from the elements of the aluminum, nickel, zirconium, and rare-earth groups the elements of all the preceding groups. The separation from the sodium salt is necessary in order to make it practicable to submit the mixture to the distillations with HBr and $HClO_4$ and to the fuming with $HClO_4$ (in P. 4–6) required for the isolation of the selenium, tungsten, tantalum, and gold groups and of osmium and ruthenium. All the elements of these groups are precipitated under the conditions prescribed in P. 71. They are brought down either by the H_2S as sulfides, or in the cases of tungsten, tantalum, and columbium, by the heating in acid solution as acidic hydroxides. Of the elements of the thallium group, silver and lead, but not thallium, are precipitated by the H_2S. As to the detection of thallium in this case see Note 5, P. 94.

7. The sulfides, even those of the platinum elements, dissolve either on heating with HBr and Br_2 or upon the subsequent addition of HNO_3. Osmium and ruthenium will therefore be found in the distillates obtained in P. 5 by heating with HNO_3 and $HClO_4$.

8. Owing to the fact that iridium and rhodium may be again precipitated by the boiling with $HCHO_2$ in P. 6 (see Note 7, P. 6), and may not be dissolved by the HNO_3 and HCl in P. 9 (see Note 1, P. 9), a residue of these metals may again remain after the acid treatment of P. 9. Such a residue is fused with a little Na_2O_2, and the melt treated as directed in the first two paragraphs of P. 11. The resulting H_2S precipitate, however, now that it presumably consists only of iridium and rhodium, is united with the main H_2S precipitate.

ANALYSIS OF THE SELENIUM GROUP

With G. Victor Sammet and Ernest H. Swift

Tabular Outline III

ANALYSIS OF THE SELENIUM GROUP

Distillate: $SeBr_4$, H_3AsO_4, $GeBr_4$, in HBr and Br_2 solution.
Add $Na_2S_2O_5$ (to reduce Br_2), *then* NH_2OHHCl; *heat* (*P. 21*).

Precipitate, red turning black: Se.	Filtrate: H_3AsO_4, $GeBr_4$. *Saturate with* H_2S, *heat* (*P. 22*).			
	Precipitate: As_2S_5 or As_2S_3 and S, GeS_2. *Treat with* NH_4OH (*P. 23*).			Filtrate. *Reject.*
	Solution: $(NH_4)_3AsO_4$, $(NH_4)_2GeO_3$, and thio-salts. *Add HF, saturate with* H_2S (*P. 23*).			
	Precipitate: As_2S_5, As_2S_3. *Dissolve in* NH_4OH, *evaporate, add* HNO_3 (*P. 24*).		Filtrate: H_2GeF_6. *Evaporate with* H_2SO_4, *dilute, add* H_2S (*P. 25*).	
	Solution: H_3AsO_4. *Add* NH_4OH *and* $Mg(NO_3)_2$.		Precipitate: GeS_2. *Diss. in* NH_4OH, *add HF, evaporate* (to remove SiO_2); *add HF,* K_2CO_3.	Filtrate. *Reject.*
	Precipitate: $MgNH_4AsO_4$. *Treat with* $AgNO_3$.	Filtrate. *Reject.*	Precipitate: K_2GeF_6.	
	Residue, red: Ag_3AsO_4.			

General Discussion

D. 21. Separation of Selenium, Arsenic, and Germanium (*P. 21–25*).—From the distillate, which contains these three elements in a hydrobromic acid solution containing free bromine, after reducing the bromine with sulfite, the selenium is separated from the arsenic and germanium by heating with hydroxylamine, which precipitates the selenium as the elementary substance, at first in its very characteristic red form.

To determine whether there is any arsenic or germanium in the filtrate, and to separate them when present from the large excess of hydrobromic acid, hydrogen sulfide is passed into the filtrate. The fairly large acid concentration (about 4 normal) is favorable

to the precipitation of both of these elements, and is essential in the case of germanium, which is very incompletely precipitated at much smaller acid concentrations (as well as at much greater ones). The hydrobromic acid can not be removed by evaporation, since the arsenic and germanium would volatilize at the same time. It can be destroyed by cautiously adding fuming nitric acid to the ice-cold distillate; but this process does not at once afford any indication as to whether any germanium or arsenic is present, and in their absence involves the unnecessary carrying out of rather lengthy operations.

To separate arsenic and germanium from each other, use is made of the process described by Müller [1] in which arsenic is completely precipitated from a hydrofluoric acid solution by hydrogen sulfide, while germanium remains in solution, doubtless owing to its conversion into the complex fluogermanic acid (H_2GeF_6). A hydrofluoric acid solution of the right concentration is obtained by dissolving the two sulfides in ammonium hydroxide and adding a measured excess of hydrofluoric acid.

From the filtrate the germanium is precipitated as sulfide by displacing the fluoride by evaporation of the mixture with sulfuric acid to fuming, adding water, and saturating the solution with hydrogen sulfide. The presence of germanium in the precipitate is finally confirmed by converting it into potassium fluogermanate (K_2GeF_6), the only other slightly soluble form in which this element can be satisfactorily precipitated. It is precipitated successively in these two forms, since this double isolation of the element affords additional evidence of its presence, since the sulfide test more quickly demonstrates its absence when it is actually not present, and since the success of this test is less dependent on close adherence to specified conditions.

Wada and Kato [2] have recently described a similar scheme of analysis, in which, however, germanium is separated from arsenic by adding concentrated nitric acid to the hydrobromic acid distillate, evaporating to dryness, and distilling the residue with concentrated hydrochloric acid in a current of chlorine. Thereby the germanium distills over, while all the arsenic remains in the flask.

[1] Müller, *J. Am. Chem. Soc.*, **43**, 2549 (1921). Müller worked only with trivalent arsenic; but quinquivalent arsenic was also found to be rapidly precipitated from solutions concentrated in hydrofluoric acid.

[2] Wada and Kato, *Sci. Papers Inst. Phys. Chem. Research*, **2**, 243–261 (1925).

ANALYSIS OF THE SELENIUM GROUP

Tabular Outline III

See page 62.

Procedures and Notes

Procedure 21.—*Precipitation of Selenium.*—To the distillate * from the HBr distillation (P. 4) in a small flask, add 1 f.† $Na_2S_2O_5$, drop by drop, till the excess of Br_2 is almost completely destroyed, as shown by the color and odor of the solution, meanwhile keeping the mixture cool. (If an excess of the $Na_2S_2O_5$ has been added, add Br_2 solution, a few drops at a time, till the color is restored.) Add 1 cc. of 3 f. NH_2OH-HCl (hydroxylamine hydrochloride), cover the flask with a watch-glass, and heat it on a steam-bath for 5 minutes (but do not boil it over a flame). If much precipitate forms, add 1 cc. more 3 f. NH_2OHHCl. Cool the mixture and filter it. (Red precipitate darkening on heating, presence of SELENIUM.)

Treat the filtrate by P. 22.

Notes.—1. $Na_2S_2O_5$, sodium bisulfite, is used to reduce the free Br_2, rather than NH_2OH (hydroxylamine), since the latter is an expensive reagent. The sulfite can not well be used for completing the reduction, nor for the precipitation of the selenium, because any excess of it would in the later treatment with H_2S cause precipitation of sulfur, which might be mistaken for GeS_2. Neither NH_2OH nor the products produced by its oxidation in this case decompose H_2S in the acid solution.

2. NH_2OH reduces selenium only slowly in cold strongly acid solution; but, when heated as directed, the precipitation is complete within five minutes. The NH_2OH is thereby oxidized to N_2O. The precipitation of the selenium in the red dispersed form in which it first separates is a very characteristic and delicate test

* For practice-analyses mix test-solutions of selenium, arsenic, and germanium (1 cc. of each) with 10 cc. of 9 n. HBr, distil the mixture into 5 cc. of Br_2 solution as described in P. 4, and analyze the distillate by P. 21–25.

† In this book the term *formal* and the symbol *f.* are used to denote formula-weights per liter.

for this element, less than 0.5 mg. giving a distinct precipitate. On heating, this form gradually changes to the much more compact black modification. Hydrochloride or sulfate of hydrazine (N_2H_4) may be substituted for NH_2OHHCl, if preferred, as it has nearly the same reducing action.

3. The solution is kept cool during the addition of the $Na_2S_2O_5$, and is afterwards heated only on a steam-bath and in a covered flask, so that germanium may not volatilize. The arsenic is not reduced by the NH_2OH to the trivalent state, and therefore there is no danger of its loss by volatilization.

4. Concentrated reagents are used in this Procedure and the addition of water is avoided so that the acid concentration may remain large enough to permit of the rapid and complete precipitation of arsenic and germanium by H_2S in the next Procedure.

Procedure 22.—*Precipitation of Arsenic and Germanium.* —Saturate the (cold) filtrate from the NH_2OH precipitate (P. 21) with H_2S in a 50-cc. pyrex bottle (adding 10–20 cc. of 6 n. H_2SO_4, if the mixture becomes thick with precipitate). While the bottle is filled with H_2S, insert a rubber stopper, and wire it securely to the neck of the bottle (or better, clamp the bottle in a pressure-bottle frame). Immerse the bottle in a vessel of water, heat the water to boiling, and boil it for 5 minutes. Let the bottle cool, open it, saturate the mixture with H_2S, stopper the bottle, and let it stand 10 minutes. (White precipitate, presence of GERMANIUM; yellow precipitate, presence of ARSENIC.) Filter the mixture with the aid of suction, wash the precipitate thoroughly with a small quantity of 6 n. H_2SO_4 saturated with H_2S, and suck the liquid out of it.

Treat the precipitate by P. 23 (see Notes 3 and 5); and reject the filtrate.

Notes.—1. The solution is saturated with H_2S in the cold and afterwards heated in a pressure-bottle, in order to completely precipitate the arsenic. This is present as H_3AsO_4, since the $AsBr_3$ that distils over is oxidized by the Br_2 in the distillate, and since the H_3AsO_4 thus formed is not reduced by the NH_2OH. The use of a pressure-bottle for the heating also avoids the loss by volatilization of germanium, whose sulfide may dissolve somewhat on heating the solution. The mixture is again saturated with H_2S in the cold, in order to ensure its complete precipitation.

2. Germanium is peculiar in the respect that it is completely precipitated in the cold from solutions moderately concentrated (4 to 6 n.) in H_2SO_4, HCl, or HBr, but not from slightly acid solutions; this behavior being probably due to the fact that, though the sulfide GeS_2 as such is very slightly soluble, the complex thiogermanate ion $GeS_3^=$ is unusually stable with respect to decomposition by hydrogen-ion. Quinquivalent arsenic is more rapidly precipitated the more concentrated the acid; but too high a concentration causes germanium to remain in solution. The precipitation is therefore made in moderately acid solution. Since GeS_2 has a great tendency to become colloidal, the precipitate is washed, not with water, but with 6 n. H_2SO_4 saturated with H_2S. The bottle is corked when it is allowed to stand, so as to keep out the air and avoid the precipitation of sulfur, which might be mistaken for GeS_2. Owing to the possibility of the separation of sulfur, a small white precipitate is not conclusive evidence of the presence of germanium.

3. If under the conditions of the Procedure no precipitate results, it shows the absence of even 1 mg. of arsenic or germanium, and it is not necessary to proceed further. If the precipitate is pure white, it shows the absence of even 1 mg. of arsenic; and in that case the precipitate need not be treated by P. 23, but it may be directly treated as described in the last paragraph of P. 25, to confirm the presence of germanium.

4. Any antimony or tin that passed over into the distillate (see Note 2, P. 4) will not be precipitated at this point owing to the large concentration of hydrobromic acid. After the treatment with NH_2OH in P. 22 the antimony will be in the trivalent state. Any tellurium that may have come over in the form of H_2Te (see Note 2, P. 2) will be here precipitated as brownish-black TeS_2, which is decomposed into black Te and sulfur when the solution is heated.

5. If it is not desired to test for germanium, any yellow precipitate may be treated directly by P. 24 to confirm the presence of arsenic.

Procedure 23.—*Precipitation of Arsenic.*—Dissolve the H_2S precipitate (P. 22) by pouring repeatedly through the filter a measured 6–18 cc. portion of 6 n. NH_4OH. To the solution in a platinum dish or bakelite beaker add 27 n. HF (see Note 3, P. 3), using a volume equal to just two thirds of that of the NH_4OH used. Cool the mixture, and saturate it

with H_2S, using a bakelite or hard-rubber tube or a glass tube coated with paraffin; and continue to pass a slow current of the gas for 5 minutes. (Yellow precipitate, presence of ARSENIC.) Filter, and wash the precipitate. Collect the filtrate in a platinum dish.

Treat the precipitate by P. 24, and the filtrate by P. 25.

Notes.—1. The solution subjected to the H_2S treatment is made about 7 n. in HF and 3.5 n. in NH_4F. Large acid concentration is essential in order to secure rapid precipitation of quinquivalent arsenic. Large fluoride concentration is required to prevent precipitation of the germanium, which it doubtless does through conversion of the simple germanium ion into the complex ion, $GeF_6^{=}$. Under these conditions 1 mg. of either of these elements is satisfactorily separated from 500 mg. of the other.

2. Any tellurium that may be present (see Note 4, P. 22) does not dissolve in the NH_4OH added at the beginning of the Procedure.

Procedure 24.—*Confirmation of Arsenic.*—Pour repeatedly through the filter containing the H_2S precipitate (P. 23) 5–10 cc. of 6 n. NH_4OH; and evaporate the solution almost to dryness. Add 2–5 cc. of 16 n. HNO_3, and heat the mixture till the residue dissolves or only sulfur remains. Evaporate the mixture almost to dryness, add 1–3 cc. of water and 1–3 cc. of 6 n. NH_4OH, and filter out any residue. Add to the solution in a test-tube 3–10 cc. of $Mg(NO_3)_2$ reagent, shake it vigorously, and let it stand 10–15 minutes with occasional shaking. (White crystalline precipitate, presence of ARSENIC.)

Filter, wash the precipitate with 2–3 cc. of water, and pour over it on the filter 1 cc. of 1 n. $AgNO_3$ to which 6–8 drops of 6 n. $HC_2H_3O_2$ have been added. (Dark-red residue, presence of ARSENIC.)

Notes.—1. The precipitate of $MgNH_4AsO_4$ is a crystalline substance which tends to form supersaturated solutions. The mixture is therefore vigorously shaken and allowed to stand.

2. The treatment of the precipitate with $AgNO_3$ serves to distinguish $MgNH_4AsO_4$ from $Mg(OH)_2$ or other hydroxide that might be precipitated by NH_4OH. The $HC_2H_3O_2$ is added to neutralize any NH_4OH adhering to the precipitate.

Procedure 25.—*Detection of Germanium.*—To the filtrate from the H_2S precipitate (P. 23) in a platinum dish add 10 cc. of 18 n. H_2SO_4, evaporate the solution till the H_2SO_4 fumes, cool it, and pour it into 25 cc. of water in a small flask. Saturate the solution with H_2S, cork the flask, and let it stand at least ten minutes. (White precipitate, presence of GERMANIUM.)

Confirmation of Germanium.—Collect the precipitate on a small filter, and wash it thoroughly with a little 6 n. H_2SO_4 saturated with H_2S. Pour repeatedly through the filter a 2–3 cc. portion of 3 n. NH_4OH, and wash it out with a little water. Transfer the solution to a platinum crucible, and evaporate it just to dryness. Add 1–3 cc. of 27 n. HF, and heat the mixture to boiling. Filter the solution if it is not perfectly clear, and again evaporate it just to dryness. Add to the residue 10 drops (0.3 cc.) of 27 n. HF, 10 drops of 6 n. K_2CO_3, and 1 cc. of water; heat the mixture to boiling, cool it, and let it stand at least 15 minutes. (Greyish-white precipitate, presence of GERMANIUM.)

Notes.—1. The quantity (10 cc.) of 18 n. H_2SO_4 added to the solution is such as to give, after evaporating to fuming and diluting with 25 cc. of water, an acid concentration of about 6 normal, which is suitable for the precipitation of germanium by H_2S from cold solutions.

2. When the original H_2S precipitate in P. 32 was white, this second precipitation with H_2S may be omitted, as stated in Note 3, Note 22, and the confirmatory test with fluoride be directly applied. This H_2S precipitation may also be omitted in other cases; but it has the advantages of isolating the germanium in two different forms, thus affording additional evidence of its presence; and of more quickly demonstrating the absence of the element in cases where it is not present. When the H_2S treatment is used and it yields a precipitate, the fluoride confirmatory test should not be omitted, since it is highly characteristic of germanium, and since a small white H_2S precipitate might consist of sulfur.

3. In the confirmatory test the HF solution is first filtered if it is not perfectly clear, in order to remove sulfur, and then

evaporated to eliminate all danger from the presence of silica, which would vitiate the germanium test by giving a precipitate of K_2SiF_6 resembling that of K_2GeF_6.

4. The K_2GeF_6 separates as a viscous-appearing, greyish-white, translucent precipitate, which may easily be overlooked by one not familiar with its appearance when it is present in small quantity. Yet with less than 1 mg. of germanium a precipitate can be seen gathered together on the bottom of the crucible and following the edge of the liquid when the crucible is slowly turned and tilted. Owing to the moderate solubility of the precipitate the solution should be as concentrated as possible.

ANALYSIS OF THE TUNGSTEN AND TANTALUM GROUPS

With Tsun Chang, Bart E. Schlesinger, and Roger Williams

Tabular Outline IV

ANALYSIS OF THE TUNGSTEN GROUP
ISOLATION OF THE TANTALUM GROUP

Residue: Sb_2O_5, SnO_2, WO_3, *MoO_3, ‡TeO_2, ‡V_2O_4, *TiO_2, Ta_2O_5, Cb_2O_5, ‡Bi_2O_3; phosphates of Sn, ‡Ti, and ‡Zr.
Dissolve in HF (P. 6), evaporate with H_2SO_4, dilute, add NH_4OH and $(NH_4)_2S$, heat in pressure-bottle (P. 30).

Filtrate: Ammonium thio-salts of Sb, Sn, W, Mo, Te, V; $(NH_4)_2HPO_4$.
Pour into dilute H_2SO_4 (P. 31).

Precipitate: Sb_2S_5, SnS_2, WS_3, MoS_3, TeS_2, V_2S_5.
Dry, ignite in H_2S gas (P. 32).

Residue and sublimate: Sb_2S_3, SnS, WS_2, MoS_2, Te, V_2S_3.
Treat with 10 cc. of 12 n. HCl (P. 32).

Filtrate: H_3PO_4, ‡H_2WO_4.
Test for phosphate; if present, evaporate, ignite, add $SnCl_2$ (P. 40).

Blue color: W_2O_5.-xWO_3.

Precipitate: TiO_2, Ta_2O_5, Cb_2O_5; Ti and Zr with PO_4 or VO_4; Bi_2S_3.

See Tabular Outline V. (*Page 76*).

Filtrate: $SbCl_3$, $SnCl_2$.
Dilute to 55 cc., add H_2S (P. 33).

Precipitate: Sb_2S_3.

Filtrate: $SnCl_2$.
Partly neutralize, add H_2S (P. 34).

Precipitate: SnS.

Residue: WS_2, MoS_2, Te, V_2S_3.
Treat with HCl and HNO_3, evaporate, boil with 2 n. HCl (P. 35).

Residue: H_2WO_4.
Dissolve in NH_4OH, evaporate, add $SnCl_2$ (P. 36).

Precipitate, blue: W_2O_5.-xWO_3.

Filtrate: H_2MoO_4, H_2TeO_3, $VOCl_2$.
Dilute, pass in H_2S, heat in pressure-bottle (P. 37).

Precipitate: MoS_3, Te.
Dissolve in HCl-HNO_3, evaporate, add HCl, KSCN, and Zn (P. 38).

Solution, red: $MoO(SCN)_3$.

Precipitate, black: Te.

Filtrate: $VOCl_2$.
Evaporate, add NH_4OH, saturate with H_2S (P. 39).

Solution, violet-red: $(NH_4)_3VS_4$.

* ‡ For the significance of these signs see page 9.

General Discussion

SEPARATION OF THE TUNGSTEN AND TANTALUM GROUPS

D. 30. Elements Present in the Hydrofluoric Acid Solution.—The hydrofluoric acid solution of the residue left undissolved by the diluted perchloric acid contains all the antimony, tin, tantalum, and columbium present in the original material; also all the tungsten, and any molybdenum present in excess of about three milligrams, except when they are associated with phosphate; also the titanium present in excess of about four milligrams, except when it is associated with zirconium. It may contain, furthermore, nearly all the titanium and zirconium when phosphate is present, and in special combinations all the vanadium and tellurium as well as all of a small quantity of bismuth. All these elements must therefore be tested for in the analysis of these two groups. On the other hand, all the elements here mentioned, except antimony, tin, tantalum, and columbium, may, even when present in large quantity, in special combinations be found wholly in the perchloric acid solution; hence they must be tested for there also. Small quantities of lead and other elements may also be carried into the residue undissolved by the perchloric acid; but probably never to so large an extent as to make it necessary to test for them here.

D. 31. Displacement of the Hydrofluoric Acid by Sulfuric Acid (P. 30).—The solution is first evaporated to fuming with sulfuric acid to remove the hydrofluoric acid, and the mixture diluted with cold water. This may cause the precipitation of tungstic acid or of phosphates of tin, zirconium, or titanium; but without filtering out any such precipitate the mixture can be directly subjected to the scheme of analysis outlined below.

D. 32. Separation of the Tungsten Group from the Tantalum Group by Ammonium Sulfide (P. 30).—The basic feature of this analysis is the digestion of the mixture with ammonium hydroxide and sulfide, whereby the elements present are separated fairly sharply into two groups. Namely, there are found in the precipitate the following elements, constituting the *tantalum group:* titanium, tantalum, and columbium (sometimes called niobium). These elements will be accompanied by any zirconium or bismuth, and part or all of the vanadium, that passed into the fluoride solu-

tion in P. 7. And there are present in the filtrate the following elements, constituting the *tungsten group:* antimony, tin, tungsten, and molybdenum. With them will be found the tellurium and part or all of the vanadium that passed into the fluoride solution.

In order to make the extraction of the soluble sulfides more complete, the mixture is digested in a pressure-bottle with ammonium hydroxide and sulfide whenever the formation of a considerable precipitate of the tantalum group makes this advantageous. Under these conditions little, if any, of the antimony, tin, tungsten, molybdenum, or tellurium remains in the precipitate; and provision for their detection in it is unnecessary. Vanadium and phosphorus, however, may be left completely in the precipitate, or may pass wholly into the sulfide solution, and must therefore be tested for in the analysis of both groups. The small quantities of tungsten and molybdenum and the vanadium that may remain in the precipitate have, to be sure, to be eliminated later in the analysis, since they interfere with the final test for columbium.

TUNGSTEN GROUP

D. 33. Precipitation of the Tungsten-Group Sulfides (P. 31).— The first step in the analysis of the tungsten group is the precipitation of its sulfides from the ammonium sulfide solution. This proved to be not so simple as it seemed; for the sulfides of some of the elements, especially of tungsten and vanadium, are very incompletely precipitated when the solution is acidified in the usual manner. It was found, however, that, by pouring the sulfide solution into an excess of 6 normal surfuric acid, at least three fourths of the tungsten and vanadium, and substantially all of the molybdenum, tellurium, antimony, and tin are precipitated. The reason why the addition of the sulfide solution to the acid gives much more complete precipitation than the reverse procedure was not determined; but it may well be that the former method precipitates the sulfides so suddenly that there is not time for the fully sulfuretted thio salts to be converted into partly oxygenated salts.

There is only one special case where the precipitation of the sulfide is not complete enough to make certain the detection of the corresponding element or to afford a reasonably reliable esti-

mate of its quantity. This is the case in which tungsten and phosphate are present together in the solution. A portion of the filtrate from the sulfide precipitate is therefore tested for phosphate (in P. 40); and, if it is found present, the rest of the filtrate is evaporated with sulfuric acid and the residue tested for tungsten with stannous chloride. This case is, however, a very rare one; for, owing to the formation of soluble phosphotungstic acid, tungsten and phosphate will not occur together in the residue from the perchloric acid treatment, unless there is also present some other element like tin to precipitate the phosphate.

D. 34. Separation of Antimony and Tin from Tungsten, Molybdenum, and Vanadium (P. 32).—It is in general advantageous to provide as soon as possible for separating the common elements of a group from the rarer ones; for in the usual case where the latter are absent this greatly shortens the process. This can be done in the tungsten group by making use of the fact that the sulfides of antimony and tin are much more soluble in hot concentrated hydrochloric acid than are those of tungsten, molybdenum, and vanadium. Unfortunately, the separation is not a sharp one when the acid is caused to act upon the sulfides in the form in which they are precipitated; for the sulfides of tungsten and vanadium are then dissolved to a considerable extent. It was found, however, that, by igniting the sulfides moderately in a current of H_2S in a combustion tube, the sulfides of the rarer elements are made entirely insoluble in hot concentrated hydrochloric acid, while those of antimony and tin are still very readily dissolved, so that the separation with this acid is then an extremely satisfactory one.

D. 35. Separation and Detection of Antimony and Tin (P. 33, 34).—Having obtained by the treatment of the ignited sulfides with strong hydrochloric acid the antimony and tin free from rarer elements, their separation and detection can be carried out by any of the processes employed in common-element qualitative analysis. The method developed by Loviton,[1] Bailey and Cady,[2] and Noyes and Bray,[3] and used by A. A. Noyes in his Qualitative Chemical Analysis, has been here adopted. This method is based

[1] Loviton, *J. Chem. Soc. London*, **54**, 992 (1888).

[2] Bailey and Cady, *Qualitative Analysis*, 5th ed., 132–6 (1905).

[3] Noyes and Bray, *J. Am. Chem. Soc.*, **29**, 203–4 (1907).

primarily on the successive precipitation of the two elements by hydrogen sulfide from solutions of carefully adjusted volume and acid concentration.

D. 36. Separation of Tungsten from Molybdenum, Tellurium, and Vanadium (P. 35).—The separation of tungsten from the other rarer elements is made by decomposing the sulfides with nitric and hydrochloric acids, evaporating the mixture with concentrated hydrochloric acid to dehydrate the tungstic acid, and then boiling the residue with 20–40 cc. of 2 normal hydrochloric acid to dissolve out the molybdenum, tellurium, and vanadium. Jannasch and Bettges [1] used this acid combined with hydrazine hydrochloride, and attributed their success to a dehydrating action of the latter on the tungstic acid during the evaporation. Our experiments show, however, that hydrochloric acid alone gives satisfactory results; thus, with a mixture of 1 mg. of tungsten and 100 mg. of molybdenum, there was a small residue which gave the confirmatory test for tungsten.

Before adopting this procedure experiments were made in the attempt to use sulfuric acid for this separation.[2, 3] It was found, on evaporating the nitric-hydrochloric-acid mixture to slight fuming with 2–3 cc. of 36 normal sulfuric acid, digesting at this temperature, and diluting with 5 cc. of water, that 100 mg. of molybdenum dissolved completely, while 2 mg. of tungsten usually gave a slight residue. These results, though fairly satisfactory, were less favorable than those with hydrochloric acid.

D. 37. Confirmation of Tungsten (P. 36).—As a confirmatory test for tungsten in the residue from the acid treatment, the production of its deep-blue reduction-product with stannous chloride was adopted, after determining the conditions under which molybdenum does not give rise to its similar blue compound nor interfere with the formation or observation of the tungsten compound.

D. 38. Separation of Molybdenum, Tellurium, and Vanadium (P. 37, 38, 39).—Molybdenum and tellurium are separated from vanadium by precipitation of the first two elements with hydrogen sulfide. As is well known, it is difficult to secure complete pre-

[1] Jannasch and Bettges, *Ber. deutsch. chem. Ges.*, **37**, 2228 (1904).
[2] Ruegenberg and Smith, *J. Am. Chem. Soc.*, **22**, 772 (1900).
[3] Hommel, Treadwell-Hall, *Quantitative Analysis*, 6th Ed., 273 (1924).

cipitation of molybdenum by this reagent; and this is desirable here, since otherwise it interferes with the most satisfactory test for vanadium—the formation of a violet-red color in ammoniacal solution with hydrogen sulfide. Molybdenum is, however, thrown down completely when the hydrochloric acid solution is diluted rather largely and saturated first in the cold with hydrogen sulfide, and then heated at a boiling temperature in a pressure-bottle. The presence of molybdenum is shown by the delicate and characteristic red coloration produced by treating its solution with zinc in the presence of thiocyanate. That of tellurium is indicated by its deposition in this treatment as the black finely divided metal; this indication being confirmed by dissolving the metal in hydrochloric and nitric acids, evaporating, and reprecipitating it with sulfurous acid and iodide. The presence of vanadium is determined by the violet-red color test just referred to, and is confirmed by the orange color it produces with hydrogen peroxide, and if need be, by precipitation as ammonium metavanadate.

MODIFICATIONS OF THE PROCESS INVESTIGATED

D. 39. Initial Removal from the Hydrofluoric Acid Solution of Some of the Elements by Hydrogen Sulfide.—It was found that by saturating a solution 3 normal in hydrofluoric acid with hydrogen sulfide all of the bismuth and tellurium and much of the molybdenum and antimony are precipitated. (If arsenic is present, it is also largely thrown down.) This method would provide a means of removing the small quantities of bismuth and tellurium that may be present; but as it causes molybdenum and antimony to divide, it was considered on the whole not advisable to adopt it as part of the scheme.

D. 40. Provision for the Detection of Arsenic (*Note 6, P. 32*).—In this system of analysis arsenic is normally removed by the distillation with hydrobromic acid (in P. 4). Nevertheless, it seemed advisable to study the behavior of this element in the procedures for the analysis of the tungsten group; for the analyst might in special cases prefer to dissolve the substance in hydrochloric and nitric acids (see D. 14), rather than in hydrobromic acid and bromine; and in that case, provided tin or tantalum-group elements were also present, arsenic would be carried into the residue undissolved by perchloric acid (in P. 6). Its pres-

ence in the tungsten group does not introduce complications; for during the ignition of the sulfides in hydrogen sulfide the sulfide of arsenic volatilizes, leaving those of tungsten, molybdenum, and vanadium in the boat, and condenses, like antimony sulfide and sulfur, on the combustion-tube somewhat removed from the heated zone. By treating the sublimate separately with concentrated hydrochloric acid, the sulfide of arsenic is left behind, and can be tested for in the usual way. Tellurium, if present, would volatilize with the arsenic sulfide, and remain with it after treatment with the acid.

Tabular Outline V

Analysis of the Tantalum Group

<table>
<tr><td colspan="5">Precipitate: TiO_2, Ta_2O_5, Cb_2O_5, Ti and Zr with PO_4 or VO_4; Bi_2S_3 (P. 30). Boil with sodium salicylate solution (P. 41).</td></tr>
<tr><td colspan="2">Filtrate: Ti salicylate, H_3VO_4, H_3PO_4. Evaporate, add H_2SO_4, extract salicylic acid with ether, add NaOH (P. 42).</td><td colspan="3">Residue: Ta_2O_5, Cb_2O_5, ZrO_2, $Zr(HPO_4)_2$, Bi_2S_3. Fuse with K_2CO_3, add cold water (P. 45).</td></tr>
<tr><td colspan="2" rowspan="2"></td><td colspan="2">Filtrate: $K_8Ta_3O_{19}$, $K_8Cb_3O_{19}$, K_2HPO_4. Saturate with SO_2, heat, filter (P. 46).</td><td rowspan="2">Residue: ZrO_2, Bi_2O_3. Fuse with $K_2S_2O_7$, add water and H_2S (P. 49).</td></tr>
<tr><td colspan="2">Precipitate: Ta_2O_5, Cb_2O_5. Dissolve in HF, add K_2CO_3, evaporate, ignite, add water, boil (P. 47).</td></tr>
<tr><td>Precipitate: TiO_2. Dissolve in H_2SO_4 and H_2O_2 (P. 43).</td><td>Filtrate: Na_3VO_4, Na_3PO_4. Add HCl, NH_4OH, and H_2S (P. 44).</td><td rowspan="4">Precipitate: $2K_2TaF_7$.-Ta_2O_5.</td><td>Filtrate: K_2CbF_5O. Fume with H_2SO_4, add NH_4OH, then H_2SO_4, filter (P. 48).</td><td>Precipitate, black: Bi_2S_3.</td><td>Filtrate: $ZrOSO_4$. Boil, add H_2O_2 and Na_2HPO_4 (P. 49).</td></tr>
<tr><td>Orange solution: TiO_2.-H_2O_2. Add Na_2SO_3 and Na_2HPO_4.</td><td>Solution, violet-red: $(NH_4)_3VS_4$.</td><td>Precipitate: Cb_2O_5. Dissolve in HF, fume with H_2SO_4, add HCl, pour through Zn column.</td><td></td><td>Precipitate: $Zr(HPO_4)_2$.</td></tr>
<tr><td>Precipitate: Ti-$(HPO_4)_2$.</td><td></td><td>Solution: $CbCl_3$. Add to $HgCl_2$ (P. 48).</td><td></td><td></td></tr>
<tr><td></td><td></td><td>Precipitate: Hg_2Cl_2.</td><td></td><td></td></tr>
</table>

The oxides shown in the table as anhydrous are in reality all hydrated, except those resulting from the fusion.

TANTALUM GROUP

D. 41. Separation of Titanium and Vanadium from Tantalum, Columbium, and Zirconium (*P. 41*).—The analysis of the tantalum group involves one of the most difficult of analytical problems. Indeed, until rather recently, no satisfactory method of separating titanium from tantalum and columbium was known. Methods which work well when the elements are present alone fail to effect a good separation when they are together. Thus fusion with potassium carbonate and extraction of the melt with cold water leaves all the titanium in the residue and causes all the tantalum and columbium to pass into solution when the respective elements are present alone; but, when titanium and columbium are present together, some of the former dissolves and some of the latter remains in the residue.[1] Similarly, the separation of the three elements in the form of the double potassium fluorides is unsatisfactory—even that of titanium and columbium, where, in spite of a considerable difference in solubility, a good separation fails because of the formation of isomorphous mixtures.[1] Furthermore, the method of separating titanium from the other two elements by fusing the oxides with potassium bisulfate and extracting with cold water the titanium sulfate while leaving tantalum and columbium oxides, is useless, since fairly large quantities of these elements also pass into solution when much titanium is present.[2]

A satisfactory solution of the problem was furnished, however, by the process developed by Hauser and Herzfeld[3] and by Müller,[4] which utilizes the fact discovered by Dittrich and Freund[5] that titanium hydroxide differs from certain other hydroxides in the respect that it dissolves in acid salicylate solution. We have found that, by applying this process to the precipitated hydroxides (instead of to the melt from a carbonate fusion) and boiling these with a large volume of a dilute solution of

[1] Meyer and Hauser, *Die Analyse der seltenen Erden und der Erdsäuren*, 288–289 (1912).

[2] Weiss and Landecker, *Z. anorg. Chem.*, **64**, 75, 87 (1909).

[3] Hauser and Herzfeld, *Zentralbl. f. Mineralogie*, **1910**, 759; Meyer and Hauser, *Die Analyse der seltenen Erden und der Erdsäuren*, 291 (1912).

[4] Müller, *J. Am. Chem. Soc.*, **33**, 1506 (1911).

[5] Dittrich and Freund, *Z. anorg. Chem.*, **56**, 344 (1907).

sodium salicylate and salicylic acid, all the titanium passes into solution, and that all the tantalum, columbium, and zirconium remain undissolved, whether the elements are present in large or small quantity, and whether they are alone or mixed. This method has therefore been adopted in this form. Any vanadium or tungsten retained by the ammonium sulfide precipitate of the hydroxides also passes into the salicylate solution; while any molybdenum, bismuth, or lead retained as sulfide remains as such undissolved.

D. 42. Detection of Titanium and Vanadium (P. 42–44).— The titanium in the salicylate solution is separated from any vanadium or phosphate present by concentrating the solution, acidifying it, extracting the salicylic acid with ether, and boiling the aqueous solution with fairly concentrated sodium hydroxide solution. Thereby the titanium is completely precipitated. The titanium is confirmed by dissolving the precipitated hydroxide in a mixture of nitric acid and hydrogen peroxide, to which it imparts its characteristic orange color. Its presence is further confirmed by the use of sodium phosphate. This reagent, when added to a peroxide solution, in the presence of a proper quantity of sulfuric acid, removes any small quantity of zirconium present, but does not precipitate the titanium; it throws down the latter element completely, however, when the peroxide is destroyed by the addition of sulfite. This very satisfactory separation of zirconium and titanium is substantially that described by Hillebrand.[1]

The filtrate from the sodium hydroxide precipitate contains the phosphate and vanadium. A portion of it is tested for phosphate with ammonium molybdate; and the remainder is used for the detection of vanadium, the color produced by hydrogen sulfide in ammoniacal solution being employed for this purpose.

D. 43. Separation of Tantalum and Columbium from Zirconium and Small Quantities of Contaminating Elements (P. 45, 46).—The salicylate precipitate may contain tantalum and columbium as hydroxides or salicylate complexes, and zirconium as phosphate, together with small quantities of bismuth, lead, and other sulfides, and of silica from the glass vessels. It is first treated with hydrofluoric, nitric, and sulfuric acids to volatilize silica, to destroy organic matter, and to convert sulfides into

[1] Hillebrand, *Bull. U. S. Geol. Survey*, **176**, 75 (1900); **700**, 173 (1919).

oxides. It is then fused with potassium carbonate, and the melt is extracted with cold water. This serves the purpose of separating the tantalum and columbium, which pass into solution as potassium hexatantalate and hexacolumbate, from the zirconium, which remains undissolved as oxide, as well as from any lead, bismuth, or copper which are also left as oxides or carbonates in the insoluble residue. The next operation consists in heating the solution on a steam-bath while keeping it saturated with sulfur dioxide.[1] This precipitates the tantalum and columbium in a fairly pure state, and retains in solution the phosphate and the small quantities of tungsten, molybdenum, and vanadium that may have reached this point.

D. 44. Separation and Detection of Tantalum and Columbium (P. 47, 48).—The tantalum and columbium are separated from each other in the form of their double potassium fluorides by a modification of processes previously described.[2] The method here used consists in dissolving the precipitated tantalic and columbic acids in hydrofluoric acid, adding a little potassium carbonate, evaporating to dryness, heating carefully, adding water, and boiling the solution. The tantalum then separates completely in the form of the oxyfluotantalate ($2\ K_2TaF_7 \cdot Ta_2O_5$), which has a very characteristic appearance, while all the columbium remains in solution as oxyfluocolumbate (K_2CbF_5O). This result is attained only when certain conditions are closely observed; but these were carefully worked out and are explicitly described in the Procedure.

From the filtrate the columbium is precipitated as columbic acid by evaporating to fuming with sulfuric acid, diluting, making alkaline with ammonium hydroxide, and reacidifying with sulfuric acid. Precipitation by ammonium hydroxide and failure to redissolve in dilute acid distinguish columbium and tantalum from other elements. (While these elements precipitate completely when present alone, it was found that several milligrams of columbium dissolve when 50–100 mg. of titanium are present, on strongly acidifying with hydrochloric acid.) The presence of co-

[1] Weiss and Landecker, *Z. anorg. Chem.*, 64, 72–74 (1909); Meyer and Hauser, *Die Analyse der seltenen Erden und der Erdsäuren*, 273 (1912).

[2] See Meyer and Hauser, *Die Analyse der seltenen Erden und der Erdsäuren*, 292, 185 (1912).

lumbium in this precipitate is confirmed by bringing it into sulfuric acid solution (with the aid of hydrofluoric acid), pouring the solution through a zinc reductor, and adding it to mercuric chloride solution. The zinc reduces the columbium from the quinquivalent to the trivalent state, and in this state it instantly reduces mercuric to mercurous chloride. Neither tantalum nor titanium show this behavior; and the other elements, such as tungsten, molybdenum, and vanadium, which might do so have been completely removed by the previous treatments.

D. 45. Detection of Zirconium and Bismuth (P. 49).—The residue from the potassium carbonate fusion, containing the zirconium, bismuth, lead, etc., is fused with potassium bisulfate, as this is a rapid method of bringing the zirconium dioxide into soluble form; and the melt is treated with water. By this process all the bismuth and lead present are left undissolved as sulfates, while the zirconium passes into solution. The lead and bismuth sulfates are converted into sulfides by treating the unfiltered mixture with hydrogen sulfide; and bismuth, which under certain conditions may be found wholly at this point, is tested for in this precipitate in the manner usual in the analysis for common elements. The presence of zirconium in the filtrate is determined by adding to it hydrogen peroxide and sodium phosphate, the peroxide serving to hold in solution any titanium present.

MODIFICATIONS OF THE PROCESS INVESTIGATED

D. 46. Partial Separation of Tantalum from Titanium and Columbium by Hydrogen Peroxide and Hydrochloric Acid.—Before the salicylate process for removing the titanium was available, a method was developed (in 1904) of isolating a large part of the tantalum nearly free from columbium and titanium. This method consists in precipitating their hydroxides by adding ammonium hydroxide to a sulfuric acid solution and digesting the mixture at 50–60° with ammonium sulfide, and then warming these hydroxides for 2–3 minutes with a mixture of 5–15 cc. of 1 formal H_2O_2 and one fifth this volume of 7 n. HCl. Under these conditions over 100 mg. of columbium or titanium dissolve readily and nearly completely; while tantalum, whether present in large or small quantity, whether alone or in mixtures, remains in large

part (about one half) undissolved. Having in this way freed the tantalum from titanium, the characteristic oxyfluotantalate test could be used to determine its presence or absence.

This method of separation was found to fail when applied to the residue obtained by evaporating an hydrofluoric acid solution just to dryness with nitric acid, or to this residue after it had been heated at 120°. Several milligrams of tantalum then dissolved completely when much titanium was present; and when present alone in small quantity columbium, like tantalum, dissolved only slightly in 5–10 minutes.

Weiss and Landecker[1] state that freshly precipitated tantalic or columbic acid dissolves readily in hydrogen peroxide, provided a base or an acid is also present; and the analytical scheme of Meyer and Hauser[2] depends on precipitating tantalic, columbic, and titanic acids by boiling a dilute sulfuric acid solution (alone or in the presence of sulfur dioxide) and dissolving them in a mixture of equal parts of 10% H_2SO_4 and 3% H_2O_2. In our experiments, however, we have never succeeded in dissolving pure tantalic acid completely in hydrogen peroxide and acid.

D. 47. Removal of Tungsten from the Tantalum Group.— Before the present plan of separation of these groups was worked out, the occlusion of tungsten in the tantalum-group precipitate produced by ammonium hydroxide and sulfide occasioned serious difficulties, both by causing loss of tungsten in the tungsten group and by interfering with the reduction test for columbium. The use of pressure-bottle digestion of the sulfide mixture reduced the proportion of tungsten included to such an extent that there is no danger of missing it in the analysis of the tungsten group; but it still interfered with the columbium test. Methods of removing it were therefore investigated. Fusion with sodium carbonate and sulfur proved satisfactory; but fusion with carbonate and nitrate did not give so good results.

[1] Weiss and Landecker, *Z. anorg. Chem.*, 64, 71, 101 (1909).

[2] Meyer and Hauser, *Die Analyse der seltenen Erden und der Erdsäuren*, 274, 302 (1912).

ANALYSIS OF THE TUNGSTEN AND TANTALUM GROUPS

Tabular Outlines IV and V

See pages 70 and 76.

Procedures and Notes

Procedure 30.—*Separation of the Tungsten Group from the Tantalum Group by Ammonium Sulfide.*—To the HF solution * (P. 7) in a platinum dish add 4 cc. of 18 n. H_2SO_4, and evaporate the mixture till the H_2SO_4 fumes strongly. Let the mixture cool, and pour it gradually into 5 cc. of cold water.

Pour the mixture into a 50-cc. resistance-glass ("pyrex") bottle, and add to it enough 15 n. NH_4OH (about 6 cc.) to make it alkaline. Then add 10 cc. of freshly prepared 6 n. $(NH_4)_2S$ reagent. Insert a cork stopper, and wire it securely to the neck of the bottle (or clamp the bottle in a pressure-bottle frame). Immerse the bottle up to its neck in a vessel of water, and heat the water to boiling. (Residue, presence of TANTALUM, COLUMBIUM, TITANIUM, ZIRCONIUM, BISMUTH, or much VANADIUM.) If there is more than a small residue (see Note 5), cool the mixture somewhat, add 10 cc. more 6 n. $(NH_4)_2S$, and continue the heating for 30 minutes with occasional shaking; then cool the bottle to room temperature by slowly adding cold water to the bath. Filter the mixture through a hardened filter with the aid of suction; wash the residue with 5–10 cc. of hot water, adding these washings to the filtrate. (In case the residue is orange or brown or very large, transfer it to a casserole, warm it for 10 minutes with 3 n. NH_4OH, and filter the mixture; boil the filtrate till most of the NH_3 is expelled, add it to the main filtrate, and heat it to 50 or 60°. See Note 7.) Then wash the residue thoroughly with hot water, rejecting the washings.

Treat the filtrate by P. 31. Treat the residue by P. 41.

* For practice-analyses use a mixture of test-solutions of antimony, tin, tungsten, molybdenum, and vanadium (1 cc. of each) with 5 cc. of 27 n. HF. Omit P. 40.

Notes.—1. The HF solution must not be evaporated to dryness before H_2SO_4 is added; for this might result in the volatilization of titanium, tantalum, and columbium, as fluorides. The HF must be completely removed, since it would attack the vessels in the subsequent operations, and would prevent the complete precipitation of the tantalum group in the treatment with NH_4OH and $(NH_4)_2S$.

2. The separation from the concentrated H_2SO_4 of a heavy yellow or greenish-yellow residue proves the presence of tungsten; a blue coloration on the sides of the dish, that of molybdenum. The absence of these indications is inconclusive.

3. Moderate quantities of all the elements of the tungsten and tantalum groups, except tungsten, remain in solution in the concentrated H_2SO_4 and in the cold diluted H_2SO_4. Tungsten, if it is present in quantity as large as 2–4 mg., separates upon dilution as a white gelatinous precipitate; if it is present in large amount, it separates as a heavy yellow or greenish-yellow powder, even before the H_2SO_4 is diluted. Columbium and tantalum, when present in large quantity, may also precipitate, especially if the liquid is allowed to become hot. When phosphate is present tungsten may not precipitate from the diluted H_2SO_4 solution, owing to the formation of phosphotungstic acid; but, on the other hand, titanium and zirconium then precipitate almost completely, and tin may precipitate partly, owing to the slight solubility of the phosphates of these quadrivalent elements.

4. If NH_4OH produces no precipitate, it proves the absence (in this solution) of tin, titanium, zirconium, tantalum, columbium, and bismuth. If no precipitate remains after the addition of the $(NH_4)_2S$, it proves the absence of all these elements except tin.

5. If after adding the NH_4OH and $(NH_4)_2S$ and heating the mixture nearly to boiling there is no residue or only a small one, the 30-minute digestion in the pressure-bottle may be omitted; for, when present alone or with only a small quantity of the tantalum group, all the elements of the tungsten group dissolve readily in the $(NH_4)_2S$ solution. The dissolving of these elements is much more complete when the precipitate is in a flocculent form (as in this Procedure) than it would be if a compact dehydrated residue, such as is obtained in P. 6, were treated directly with NH_4OH and $(NH_4)_2S$.

6. In the treatment with $(NH_4)_2S$ the various elements behave as follows. Tantalum, columbium, titanium, zirconium, and bis-

muth are completely precipitated. When present alone, at least 500 mg. of tin or antimony, at least 250 mg. of tungsten, 100 mg. of molybdenum, and 100 mg. of tellurium dissolve when 20 cc. of the $(NH_4)_2S$ reagent have been added, either in the cold or after heating in the pressure-bottle; but of 100 mg. of vanadium a large part may remain undissolved as a brown or black residue after the pressure-bottle treatment. When as much as 500 mg. of tin is present as phosphate, a small part of it may remain undissolved. When much molybdenum is present, some of it may be precipitated as yellow or red ammonium thiomolybdate; but this dissolves (rather slowly) on thorough washing of the residue with hot water.

When there is a large residue of tantalum-group elements, the heating under pressure is essential in order to extract the tungsten and molybdenum. When even 200 mg. of tungsten or 100 mg. of molybdenum are present with 100 mg. of tantalum, columbium, or titanium, the tungsten or molybdenum is nearly all extracted; and when only 2 mg. of tungsten or 1 mg. of molybdenum is present with 100 mg. of the tantalum-group elements, enough tungsten or molybdenum passes into the $(NH_4)_2S$ solution to ensure its subsequent detection. Even a large quantity of vanadium may be completely retained in the residue when it contains much titanium; and vanadium is therefore tested for in both the tungsten and tantalum groups.

7. The digestion with NH_4OH, recommended when the residue is large or colored, serves to remove tungsten-group elements, especially molybdenum and vanadium, more rapidly and completely than does washing upon the filter with hot water. A brown or black vanadium residue may pass largely into the wash-water or into the NH_4OH as a colloid; but this may be mixed with the main $(NH_4)_2S$ filtrate even though a clear solution does not result.

TUNGSTEN GROUP

Procedure 31.—*Precipitation of the Tungsten Group as Sulfides.*—Note the color of the $(NH_4)_2S$ filtrate (P. 30), and pour it, a little at a time, into 30 or 40 cc. of 6 n. H_2SO_4 (according as 10 or 20 cc. of 6 n. $(NH_4)_2S$ were used in P. 30), shaking the mixture during the addition and for a minute or two afterwards. (Coagulated yellow, orange, or black precipitate, presence of TUNGSTEN GROUP.) Filter the mixture with the aid of suction through a perforated porcelain crucible containing a mat of asbestos-felt (see Note 4). Wash the precipitate with hot water, suck the water out as completely as possible, and dry it in a hot closet at 100–125°.

Treat the filtrate by P. 40. Treat the precipitate by P. 32.

Notes.—1. If the $(NH_4)_2S$ solution after heating and filtering off the tantalum group does not have an orange or red shade, it shows the absence of molybdenum and vanadium, and makes it unnecessary to test further for these elements (in P. 37–39). As little as 1 mg. of molybdenum gives an orange color noticeably different from the pure yellow color produced by sulfur; and as little as ½ mg. of vanadium gives a distinct red color. When present in large quantity, molybdenum gives a deep red color, and vanadium a dark-red color. The color given by the molybdenum is much less pronounced before the heating (in P. 30). The other elements, tin, antimony, tungsten, and tellurium, give no characteristic color to the solution.

2. The $(NH_4)_2S$ solution is added to an excess of the 6 n. H_2SO_4, instead of being slightly acidified by adding the acid to it, since the former procedure causes a far more complete precipitation of the sulfides of tungsten and vanadium. Indeed, unless this method of mixing is adopted, almost all the tungsten and half the vanadium may remain in solution. Even under these conditions as much as 25% of the tungsten and 15% of the vanadium (but scarcely any of the molybdenum) may pass into the filtrate when large quantities of these elements are present (the filtrate being colored yellow when it contains 1 mg. or more of tungsten). These elements can, however, always be detected in the precipitate in the subsequent analysis; for, even when only 2 mg. of tungsten, 1 mg. of molybdenum, or ½ mg. of vanadium is present alone, at least three fourths of this quantity of the

element comes down in the precipitate. This is not true of tungsten, however, when much phosphate is present; for it may then pass wholly into the filtrate, yielding a colorless solution. The filtrate is therefore tested (in P. 40) for tungsten, when phosphate is found in it.

3. Even 1 mg. of tin gives with H_2SO_4, after stirring, a coagulated yellow precipitate which is readily distinguished from the fine pale yellowish-white precipitate of sulfur which the $(NH_4)_2S$ reagent itself gives. 1 mg. of antimony gives a precipitate with a still more pronounced color of orange shade; and 1 mg. of tungsten, molybdenum, tellurium, or vanadium gives a distinctly darkened precipitate. It is therefore not necessary to analyze further for any of the elements of the tungsten group when the precipitate does not coagulate and has a pale yellowish-white color.

4. The asbestos used for making the filter should previously have been strongly ignited to burn off any organic matter, since otherwise this would blacken in the subsequent ignition in H_2S and make it difficult to decide whether any element of the tungsten group is present in the residue; and it should then be thoroughly washed with 6 n. HCl and with water. The asbestos filter should be made by pouring a dilute suspension of fine asbestos fibres through the crucible, applying suction at the same time till a compact mat only about 1 mm. thick is produced. In case the filtration proves to be extremely slow, as may happen when much tin is present owing to the tendency of its sulfide to clog the filter, it is well to substitute a perforated filter-plate for the perforated crucible, so as to give a larger filtering surface.

Procedure 32.—*Separation of Antimony and Tin from Tungsten, Molybdenum, and Vanadium.*—Separate the dried H_2SO_4 precipitate (P. 31) from most of the asbestos, crush it to a fine powder if the quantity of it is large, and transfer it to a broad porcelain boat 6 cm. long.

Set up an apparatus as follows. Support on the ring of a stand a U-shaped trough of sheet-iron 15 cm. long and 2 cm. deep. Attach the trough securely to the ring by copper wires put through small holes in the trough. Line the trough completely with asbestos paper. Place in it a " pyrex " combustion tube 30 cm. long, so that one end of it projects 10 cm. beyond the trough. Insert in each end of the tube a rubber stopper

with a glass tube passing through it, and connect the shorter end through a gas wash-bottle to a H_2S generator. Provide a loosely fitting cover for the trough consisting of thick asbestos paper, and a gas-burner equipped with a wing-top.

Place the boat containing the precipitate in the combustion tube, and pass through the tube a moderately rapid current of H_2S gas. After the air has been displaced, pass the H_2S slowly, and heat the trough under the boat, gradually raising the temperature till the lower part of the boat has in a dim light only a dull-red glow. Continue the heating at this temperature (500–600°) for 10–30 minutes (according to the amount of the precipitate). Let the tube cool while the H_2S is still passing through it, and then take out the boat. (Black residue in the boat, presence of ANTIMONY, TIN, TUNGSTEN, MOLYBDENUM, or VANADIUM; black sublimate, presence of ANTIMONY, TIN, or TELLURIUM.)

In case there is no black residue in the boat and no sublimate near the heated zone, proceed no further.

In case there is a black residue or there is a sublimate near the heated zone, transfer the residue with the asbestos to a test-tube, also the boat itself if much residue adheres to it. Stopper one end of the combustion tube, pour into it just 10 cc. of 12 n. HCl, loosen the sublimate by rubbing it, and pour the contents into the test-tube containing the residue from the boat. Place the tube in a beaker of water, heat the water till the contents of the tube begin to bubble, and then keep the water for ten minutes at a temperature which causes only slight bubbling in the tube, stirring its contents from time to time. (Black residue, presence of TUNGSTEN, MOLYBDENUM, TELLURIUM, or VANADIUM.) Add 3 cc. of water, and filter the mixture. Wash the residue, adding the first washings to the filtrate.

Treat the residue by P. 35. Treat the filtrate by P. 33.

Notes.—1. The precipitated sulfides are ignited so as to make those of tungsten and vanadium insoluble in the hot 12 n. HCl, which is later used for the separation of these elements and molybdenum and tellurium from antimony and tin; for the sulfides

of tungsten and vanadium, when moist, or even when dried at 100–120°, dissolve to a considerable extent upon heating with strong HCl. A current of H_2S is passed during the ignition to prevent conversion of the sulfides into oxides. They are heated within a combustion tube, instead of within a covered crucible, so that any sulfide volatilized may be collected as a sublimate. A temperature as high as a dull-red heat is applied and the heating is prolonged for 10–30 minutes, so as to reduce the SnS_2 to SnS; for ignited SnS_2 is only very slowly dissolved by HCl, and any that failed to be reduced would dissolve only slightly, and would afterwards pass into the HNO_3-HCl solution with the rarer elements.

2. The different elements behave in the ignition as follows. Tungsten, molybdenum, and vanadium remain completely in the boat in the state of the black sulfides WS_2, MoS_2, and V_2S_3. The red Sb_2S_5 changes in the boat to the black form of Sb_2S_3, and volatilizes partly, or sometimes completely when a small quantity is present, condensing as a black sublimate, or sometimes partly as an orange sublimate. SnS_2 is converted into the black non-volatile SnS, which remains in the boat; but a small quantity of SnS_2 may volatilize before this reaction is complete, condensing as a yellow sublimate which usually changes almost completely to black SnS. Tellurium is largely volatilized, yielding a black sublimate of Te extending from the boat to the cooler part of the tube. The excess of sulfur condenses as a light-yellow sublimate, part of which may melt forming reddish drops. The sublimates increase in volatility in the order SnS_2, Sb_2S_3 and Te, sulfur; and deposit further from the heated zone in this order.

3. The ignition-products of the sulfides of tungsten, molybdenum, tellurium, and vanadium are entirely undissolved by warm 12 n. HCl, so that even 1 mg. of any of these elements yields a residue, even in case it was previously associated with a large quantity of tin or antimony. If no black residue can be seen in the boat after the ignition, and if no black residue remains after the treatment with HCl, it shows the absence of these rarer elements.

4. All the antimony is dissolved by the HCl; and all the tin is dissolved by the acid if it has been completely converted into SnS; but some of the tin may be left as a lustrous yellow powder if it is still in the state of SnS_2.

5. In case there is no black residue in the boat and there is doubt whether the sublimate consists only of sulfur, this may be determined by testing the solubility of the sublimate in CS_2 as

follows. Insert a cork stopper in one end of the combustion-tube, pour into it 5 cc. of CS_2, and loosen the sublimate by rubbing it with a rubber-capped rod. If there is still a residue, decant the CS_2 solution, evaporate that still adhering to the tube by heating it in a steam-bath, heat the residue with 12 n. HCl, and test the solution for antimony and tin by P. 33 and 34.

6. Arsenic will not in general be present here, since it was distilled off with the HBr in P. 4. Its behavior in this Procedure may, however, be mentioned, since it may sometimes be desired to analyze a residue of oxides that might contain it. In this Procedure, if arsenic were present, all of it would be volatilized in the prolonged heating, thus separating it completely from tungsten, molybdenum, and vanadium; and it would condense as a yellow sublimate of As_2S_3 somewhat removed from the heated zone, it being more volatile than Sb_2S_3 and less volatile than sulfur.—In case arsenic may be present, the sublimate is treated with 12 n. HCl separately from the residue, so as not to reunite the arsenic with the tungsten, molybdenum, and vanadium. A short heating of the sublimate with the acid suffices to dissolve the Sb_2S_3 and SnS in this case, since they are not mixed with other sulfides as they are in the residue in the boat nor with sulfur as they are when precipitated from a $(NH_4)_2S$ solution in the usual common-element analysis. The solution is kept saturated with H_2S, since otherwise the As_2S_3 slowly dissolves. Any residue undissolved by the 12 n. HCl is tested for arsenic by P. 24. In case tellurium may be present in this group with arsenic, the filtrate from the $Mg(NO_3)_2$ precipitate may be tested for this element as described in the last sentence of P. 38.

Procedure 33.—*Separation of Antimony and Tin, and Detection of Antimony.*—Dilute the HCl solution (P. 32) with water to a volume of just 55 cc.; transfer it to a flask placed in a beaker of boiling water; and, after the solution has become hot, pass into it a moderate current of H_2S gas for 8–10 minutes but no longer, keeping the water in the beaker gently boiling. (Orange-red precipitate, presence of ANTIMONY.) Filter while hot, using suction if the precipitate is large, and wash the precipitate with hot water.

Treat the filtrate by P. 34.

Transfer the precipitate to a small casserole, heat it with 2–5 cc. of 12 n. HCl, add 2–5 cc. of water, filter, and evaporate

the filtrate to about 2 cc. Cool the solution, and place in it a flat piece of bright tin. After 5–10 minutes pour off the liquid, wash the residue carefully with water by decantation, and pour over it 2 cc. of fresh NaBrO reagent (see Note 3). (Black residue remaining undissolved, presence of ANTIMONY.)

Notes.—1. By following carefully the directions given in P. 32 and in this Procedure, a good separation of antimony and tin may be attained. If, however, the HCl solution be more concentrated, a small quantity of antimony may escape detection; while, if it be more dilute or if it be not kept hot, some tin may precipitate when a large amount is present.

2. The confirmatory test is so delicate that even 0.1–0.2 mg. of antimony can be detected. It produces on the tin a coal-black color, which distinguishes it from copper, which forms a red or reddish-brown deposit. The treatment with NaBrO distinguishes antimony from arsenic and tellurium; for the last two, if present, dissolve, while antimony is unattacked.

3. Since hypobromite solution rapidly decomposes, with formation of bromate and bromide, the reagent should be prepared when needed by adding to 2 cc. of saturated Br_2 solution, 6 n. NaOH, drop by drop, till the solution becomes light yellow, and then adding as many drops more of 6 n. NaOH.

Procedure 34.—*Detection of Tin.*—To the filtrate from the H_2S precipitate (P. 33) add just 6 cc. of 15 n. NH_4OH, cool the mixture, saturate it with H_2S, cork the flask, and let it stand for 10 minutes. (Brown or yellow precipitate, presence of TIN.)

In case H_2S has produced a precipitate, evaporate the mixture (without filtering it) in a casserole to 15–20 cc., or further if the precipitate has not dissolved. Add ½ cc. of powdered antimony, and boil the mixture gently for 2–3 minutes. Filter, and to the filtrate add at once 2–3 cc. of 6 n. HCl and 10 cc. of 0.2 n. $HgCl_2$. (White or grey precipitate, presence of TIN.)

Notes.—1. The tin usually is mainly in the stannous state, in which case it yields a brownish-black precipitate of SnS. It may, however, be partly or wholly in the stannic state, owing to presence of SnS_2 in the sublimate (in P. 32) or owing to oxidation

of the stannous tin by the oxygen of the air; and in this state it produces with H_2S a yellowish translucent turbidity, or in larger quantity a yellow flocculent precipitate of SnS_2. The acid present is partially neutralized with NH_4OH and the solution is cooled, so as to ensure the complete precipitation of the sulfides, especially of SnS, which is more soluble than SnS_2. Time is allowed for the precipitation, because SnS_2 is formed rather slowly.

2. In the confirmatory test the precipitate is not filtered off, but is dissolved by concentrating the acid by evaporation, since it may clog the filter or pass through it. The $HgCl_2$ reagent is added to the solution as soon as it is filtered from the antimony, since $SnCl_2$ oxidizes rapidly in the air. The HCl is added to prevent the precipitation of SbOCl.

3. Metallic antimony is used, rather than zinc or iron, to reduce the tin from the stannic to the stannous condition, since antimony does not reduce the tin to the metallic state and since it is only slowly dissolved by boiling HCl.

Procedure 35.—*Separation of Tungsten from Molybdenum, Tellurium, and Vanadium.*—To the residue undissolved by HCl (P. 32) in a casserole add 2–4 cc. of 12 n. HCl and 2–4 cc. of 16 n. HNO_3, warm the mixture, and evaporate it almost to dryness. Add 5 cc. of 6 n. NH_4OH, warm the mixture, filter off the asbestos, and wash it out with a little water. Evaporate the solution just to dryness. To the residue add 5–10 cc. of 12 n. HCl, cover the casserole, and heat it for 5–10 minutes on a steam-bath; then evaporate the solution to complete dryness, taking care not to overheat the dry residue. Add 20–40 cc. of 2 n. HCl, and boil the mixture gently, with stirring if necessary, for about 5 minutes. Filter the mixture. (Yellow residue, presence of TUNGSTEN.) Wash the residue.

Treat the residue on the filter and that adhering to the casserole by P. 36.

Treat the filtrate by P. 37–39, omitting the tests for molybdenum and vanadium in case the $(NH_4)_2S$ filtrate (P. 30) had no noticeable orange or red shade (see Note 1, P. 31).

Notes.—1. The treatment with HCl and HNO_3 converts the WS_2, MoS_2, Te, and V_2S_3 into H_2WO_4, H_2MoO_4, H_2TeO_3, and H_3VO_4. The H_2WO_4 remains as a bright yellow residue, and

the other acids pass into solution. When, however, much molybdenum is present, as much as 2–4 mg. of tungsten may remain in solution. The heating and evaporation to dryness with 12 n. HCl dehydrate the H_2WO_4 and make it less soluble in acids. The subsequent boiling with 20–40 cc. of 2 n. HCl serves to dissolve the molybdenum. By this treatment 100 mg. of molybdenum are dissolved, while 1 mg. of tungsten yields a yellow residue, even when 100 mg. of molybdenum or vanadium are also present. By the action of the concentrated HCl the H_3VO_4 is reduced to $VOCl_2$, which gives a blue color to the 2 n. HCl solution.

2. The residue from the treatment with HNO_3 and HCl is treated with NH_4OH, since this base dissolves readily the hydrated oxides of all these rare elements and enables the asbestos fibres likely to be mixed with them to be separated from them by filtration.

3. Owing to the presence of phosphate, tungsten may have passed into the $HClO_4$ solution (see Note 4, P. 6), or into the filtrate from the H_2SO_4 precipitate of the tungsten group (see Note 2, P. 31). Failure to detect it at this point therefore does not show its absence in the original material.

Procedure 36.—*Confirmation of Tungsten.*—Dissolve the residue insoluble in HCl (P. 35) by pouring repeatedly through the filter a portion of 2–4 cc. of 15 n. NH_4OH and collecting it in the casserole previously used. Wash out the filter with 2–3 cc. of water. Evaporate the solution almost to dryness. Add 3 cc. of 1 n. $SnCl_2$, heat the mixture to boiling, and stir it. Then add 3 cc. of 12 n. HCl, heat the mixture to boiling, and let it stand until it is cool. If the mixture has an orange color, filter it, and wash out the filter with dilute HCl. (Blue precipitate, presence of TUNGSTEN.)

Notes.—1. Under the conditions described in this Procedure, even 0.5 mg. of tungsten produces a blue color, and the tungsten is almost completely precipitated within a few minutes in the form of "tungsten blue," which is probably a tungstate of quinquivalent tungsten; while molybdenum gives an orange-red solution of $MoCl_3$, but does not interfere with the precipitation of the tungsten. When enough molybdenum is present to give the mixture an orange color, it is filtered so that the deep blue color of the tungsten may be readily seen.

2. This test for tungsten would be more delicate if the solid

$(NH_4)_2WO_4$ obtained by evaporation, or the H_2WO_4 on the filter were treated with a cold solution of $SnCl_2$ in 12 n. HCl (instead of with the reagent which is 2 n. in HCl); but in this case molybdenum also produces a deep-blue compound ("molybdenum blue"), which is probably a molybdate of quinquivalent molybdenum analogous to the tungsten compound. This molybdenum blue, when once formed, is not readily reduced to the orange solution on standing with $SnCl_2$, but remains as a blue precipitate or as a blue or green colloid, which obscures the test for tungsten. When, however, the acid concentration is initially low, as in the Procedure, the $SnCl_2$ reduces the molybdate without formation of the blue compound; but since a brown precipitate may then result, 12 n. HCl is subsequently added, so as to produce a clear orange-colored solution of $MoCl_3$. When phosphate is present, as in P. 40, the blue tungsten color appears slowly, and the concentration of the HCl may be high during the reduction with $SnCl_2$ without danger of forming molybdenum blue.

Procedure 37.—*Separation of Molybdenum and Tellurium from Vanadium.*—To the HCl solution (P. 35) add three times its volume of water, and saturate it in the cold with H_2S. (Black precipitate, presence of MOLYBDENUM or TELLURIUM.) If H_2S produces a precipitate, transfer the mixture to a pyrex bottle of a capacity not much greater than the volume of the solution, saturate it with H_2S, stopper the bottle, wiring in the stopper, immerse it up to the neck in a vessel of water, and boil the water for 30 minutes. Cool the mixture by adding cold water to the bath, and filter it.

Treat the precipitate by P. 38. Treat the filtrate by P. 39.

Notes.—1. Even 1 mg. of molybdenum or tellurium gives a precipitate with H_2S in the cold; so that, when no precipitate forms, it shows that these elements are not present in this solution, and the analyst may pass directly to P. 39. When however molybdenum is present, it is only partially precipitated by H_2S in the cold, or even at the boiling temperature in an open vessel, and it must be removed by further treatment, since it interferes with the color test for vanadium in P. 39. It is only under special conditions that the last 5 or 10% of the molybdenum can be brought down by H_2S within a short time; but by first saturating a dilute HCl solution with H_2S in the cold and then heating it in a pressure-bottle, whereby the H_2S in the solution is kept at

high concentration, complete precipitation is secured in 30 minutes. Before treating it with H_2S the 2 n. HCl solution from P. 35 is diluted with three volumes of water, since a HCl concentration of 0.5 n. is favorable for the precipitation of molybdenum.

2. If any of the ignited Sb_2S_3 or SnS_2 remained undissolved by the 12 n. HCl treatment of P. 32, it would separate as an orange or yellow precipitate at this point.

Procedure 38.—*Detection of Molybdenum and Tellurium.* —Warm the H_2S precipitate (P. 37) with 1–2 cc. of 16 n. HNO_3 and 3–6 cc. of 12 n. HCl, and evaporate the mixture just to dryness. Add to it 1 cc. of 6 n. HCl and 5 cc. of water, heat the mixture to boiling, and filter out any residue. Cool the filtrate, and add to it 5 cc. of 1 n. KSCN solution. (If there is a deep red color, make the solution alkaline with 6 n. NaOH, heat it nearly to boiling, filter out the precipitate, neutralize the solution with 6 n. HCl, and add 1 cc. more.) Add about 0.2 cc. of finely granulated Zn. (Red coloration increasing for some minutes, presence of MOLYBDENUM; black precipitate, presence of TELLURIUM.)

If there is a black precipitate, add 0.5 cc. more zinc and 1 cc. of 6 n. HCl, and let the action continue till nearly all the Zn has dissolved, adding more HCl if necessary. Then filter out the precipitate, wash it, and dissolve it by warming it with 2–4 cc. of 12 n. HCl to which 5–10 drops of 16 n. HNO_3 are added. Evaporate the solution just to dryness, dissolve the residue in 5 cc. of 6 n. HCl, and add to the solution 0.2–0.5 g. of powdered Na_2SO_3, 5 cc. of water, and about 10 drops of 1 n. KI. (Black precipitate, presence of TELLURIUM.)

Notes.—1. The red color is due to the formation of a thiocyanate of quinquivalent molybdenum, to which the H_2MoO_4 is first reduced by the Zn. The test is sensitive even to 0.1 mg. of molybdenum. The intensity and the duration of the color developed may give some idea of how much molybdenum is present when the quantity is small; but the amount of the element is more conveniently and accurately estimated from the H_2S precipitate obtained in P. 37. Long-continued action of zinc causes the red color to disappear; for molybdenum in the trivalent state, to which it is finally reduced by Zn, gives a nearly colorless solution with

KSCN. A faint red color may appear before the addition of Zn, owing to reduction of the molybdenum by organic impurities.

2. Ferric salts also give an intense red color with KSCN; but the coloration in such a case appears immediately on the addition of KSCN and fades after the introduction of Zn. When as much as 1 mg. of iron is present, however, it seriously interferes with the test, and the iron is therefore removed by precipitation with NaOH. The slight amount that may still remain in the solution then gives only a faint color which after the addition of Zn disappears in less than 30 seconds.

3. The tellurium, together with any antimony or tin present, is precipitated by the Zn as the finely-divided metal. When a black precipitate results, more Zn and 6 n. HCl are added to the mixture to ensure the complete precipitation of tellurium.

4. The reduction of quadrivalent tellurium by H_2SO_3 alone in HCl solution is a very slow reaction, especially when the HCl concentration is greater than 6 or 7 n. or less than 1 or 2 n. However, in 2–4 n. HCl the reaction is rapid at room temperature in the presence of KI. The KI acts as a catalyst, probably by formation of TeI_4 (or $TeI_6^=$), which is more rapidly reduced by H_2SO_3 than is $TeCl_4$ or H_2TeO_3. If any selenium were present, some of it would be precipitated by H_2SO_3 in the 6 n. HCl solution (before the water and KI are added), and the precipitation could be made complete by warming the solution.

Procedure 39.—*Detection of Vanadium.*—Evaporate the filtrate from the H_2S precipitate (P. 38) just to dryness. To the residue add 1–2 cc. of 16 n. HNO_3, and evaporate again just to dryness. Then add 5 cc. of 6 n. NH_4OH, pour the solution into a test-tube, and saturate it completely with H_2S. (Violet-red color, presence of VANADIUM.)

If the solution is colorless, reject it.

If the solution is violet-red, evaporate the solution (without filtering) to dryness, and ignite the residue till the ammonium salts are expelled. Warm the residue with 1–2 cc. of 16 n. HNO_3, add 3 cc. of water; and if there is a residue, heat the mixture to boiling. Cool it, and add to it 1 cc. of 1 f. H_2O_2. (Orange-red color, presence of VANADIUM.) (See Note 4.)

Notes.—1. The filtrate from the H_2S precipitate shows, especially after it is concentrated to a small volume, the blue color of

$VOCl_2$ when more than 2 or 3 mg. of vanadium are present. This color is an indication of the presence of vanadium; for though molybdenum when partially precipitated with H_2S may give rise to a blue color, complete precipitation of this element should have been attained under the conditions of P. 38. The residue after the evaporation is treated with HNO_3 to oxidize the vanadium to H_3VO_4, since otherwise some of it may precipitate on the addition of the NH_4OH.

2. An ammoniacal solution of a vanadate or hypovanadate gradually becomes orange-red when H_2S is led into it; but the characteristic violet-red color results only when the solution is completely saturated with H_2S. 0.1 mg. of vanadium can then be easily detected, provided ammonium salts are present only at small concentration. Owing to the great intensity of the color, it is difficult to estimate the quantity of vanadium when more than 1–2 mg. of it is present. In such a case the estimation may be made as stated in Note 4, or by taking an aliquot part of the ammoniacal solution, diluting it with 3 n. NH_4OH, saturating it with H_2S, and comparing the color with that of a standard. When much vanadium is present, some of it may separate as a brown precipitate; but this does not obscure the violet-red color.

3. Molybdenum, if not completely precipitated by H_2S in P. 37, also gives a deep-red color with H_2S in the ammoniacal solution. The further test with H_2O_2 serves to distinguish this element from vanadium, since molybdenum, even in large amount, gives with H_2O_2 a pure yellow color, not an orange or red one. In this H_2O_2 test 0.1–0.2 mg. of vanadium may be detected in a volume of 5 cc., provided the solution is fairly acid (2–6 n.) and a large excess of H_2O_2 is avoided.

4. When the preceding tests indicate the presence of more than 0.5 mg. of vanadium, its presence may be confirmed and its quantity estimated by precipitating it as NH_4VO_3, as described in the last paragraph of P. 106.

5. Vanadium will in most cases pass into the $HClO_4$ solution in P. 6 and be detected in P. 106. Any of it that is precipitated with the tungsten and tantalum groups (see Note 3, P. 6) may divide itself between the $(NH_4)_2S$ solution and residue (see Note 6, P. 30). It is therefore also tested for in P. 44.

Procedure 40.—*Detection of Phosphate and Tungsten in the Filtrate from the Sulfuric Acid Precipitate of the Tungsten Group.*—Boil one tenth of the H_2SO_4 solution (P. 31) till the

H_2S is expelled, and filter off any residue. Pour the solution into a clear mixture of 5 cc. of $(NH_4)_2MoO_4$ reagent and 5 cc. of 6 n. HNO_3 heated to about 70°, and let the mixture stand 5–15 minutes. (Yellow precipitate, presence of PHOSPHATE.)

In case phosphate is found present, evaporate the solution in a casserole until dense fumes of H_2SO_4 are evolved. Cool the casserole, add cautiously 1 cc. of 16 n. HNO_3, and heat the mixture till the H_2SO_4 fumes; repeating these operations if organic matter is still present. Then evaporate the mixture to dryness, add 1 cc. of 12 n. HCl, and again evaporate it just to dryness. Finally add 3 cc. of 1 n. $SnCl_2$ reagent, stir the mixture, and heat it to boiling. Then add 3 cc. of 12 n. HCl, and heat again for a minute or two. If the mixture is not blue, but has an orange, brown, or green color, let it stand for several hours. (Intense blue color, presence of TUNGSTEN.)

Notes.—1. The failure of the test at this point does not prove the absence of phosphate in the tantalum and tungsten groups, since it may be carried into the $(NH_4)_2S$ precipitate (in P. 30) as titanium or zirconium phosphate. For this reason it is also tested for in the analysis of the tantalum group (in P. 44 and 46). Moreover, phosphate usually passes into the $HClO_4$ solution in P. 6, and is then detected in P. 91.

2. Although tungsten is never completely precipitated from the $(NH_4)_2S$ solution by H_2SO_4 in P. 31, the greater part of it will be found in that precipitate and be later detected in P. 35 except when phosphate is present (see Note 2, P. 31). Accordingly tungsten is tested for here only when phosphate is found here.

3. In the tungsten test HNO_3 is added to oxidize the tungsten to tungstate, and to destroy any organic matter that may be present. The evaporation with 12 n. HCl removes the HNO_3, and reduces any vanadate partially or completely to $VOCl_2$; and a green or blue color then shows the presence of vanadium even when only 2 or 3 mg. are in the solution.

4. As to the $SnCl_2$ test for tungsten, see Notes 1 and 2, P. 36. The phosphate, which is present in this case, tends to cause the tungsten to form a blue solution rather than a blue precipitate. It delays the production of the color when molybdenum or vanadium, and especially when a mixture of them, is also present; but with the small amounts of these elements that can be in this solution 1 mg. of tungsten shows itself within a few hours.

TANTALUM GROUP

Tabular Outline V

See page 76.

Procedure 41.—*Separation of Titanium and Vanadium from Tantalum, Columbium, Zirconium, and Bismuth.*—Transfer the residue * undissolved by $(NH_4)_2S$ (P. 30) to a one-liter round-bottom flask containing 350–400 cc. of hot water to which just 30 cc. of 3 n. Na_2CO_3 and 15 g. of solid salicylic acid have previously been added. Boil the mixture for two hours (unless before that time the residue wholly or nearly wholly dissolves), replacing the water which evaporates. (Residue, presence of TANTALUM, COLUMBIUM, ZIRCONIUM, or BISMUTH.) Filter with the aid of suction through an HF-washed filter, bringing the solution to boiling each time before pouring it onto the filter. (Colorless filtrate, absence of TITANIUM.) Wash the residue thoroughly with hot water.

Treat the filtrate by P. 42. Treat the residue by P. 45.

Notes.—1. The boiling salicylate solution, which is approximately 0.2 n. in sodium salicylate ($C_6H_4(OH)COONa$) and 0.04 n. in salicylic acid, dissolves only an inappreciable amount of tantalum or columbium; or of zirconium, whether it is present as hydroxide or (as is likely to be the case) as phosphate. When even 1 mg. of tantalum or columbium is present, alone or with titanium, the solution has a distinctly turbid appearance, especially during the early part of the boiling. Any residue that remains after the long boiling filters readily.

2. Titanium dissolves in large amount (at least 200 mg.) in the salicylate solution, owing to the formation of a soluble complex in which titanium or an oxytitanium radical (such as TiO^{++}) has replaced the hydrogen of the phenol group of the salicylate. The solution is colored orange-yellow by even 0.3 mg. of titanium and deep orange-red by 25 mg. The long boiling serves to extract the

* For practice-analyses this residue may be obtained by mixing 1 cc. of test-solutions of titanium, vanadium, tantalum, and columbium with 4 cc. of 18 n. H_2SO_4; evaporating till the H_2SO_4 fumes strongly; cooling; adding 5 cc. of water, enough 15 n. NH_4OH to make the mixture alkaline, and 10 cc. of 6 n. $(NH_4)_2S$ reagent; heating in a pressure-bottle in boiling water 30 minutes (as in P. 30); filtering off the precipitate; and washing it thoroughly with hot water. Omit P. 49.

titanium almost completely from a residue containing much tantalum or columbium; thus, when only 1 mg. of titanium is present with 100 mg. of tantalum or columbium, about 0.5 mg. goes into solution, while with larger amounts of titanium the unextracted quantity usually does not exceed 1–2 mg., and this introduces no later complications. The presence of phosphate in the solution does not affect the separation of even a large amount of titanium from tantalum, columbium, and zirconium.

3. Any vanadium that was in the residue from the $(NH_4)_2S$ treatment (see Note 6, P. 30) now passes into the salicylate solution with the titanium. Any molybdenum left in that residue as thiomolybdate because of incomplete washing dissolves at first, but decomposes with deposition of brown sulfide during the boiling. Any tungsten left with the tantalum group in the $(NH_4)_2S$ extraction (in P. 30) will probably pass into the salicylate solution, since H_2WO_4 alone is readily soluble in this reagent.

4. Any sulfides of elements of the copper group, such as bismuth or lead, carried into the original residue of the tungsten and tantalum groups (in P. 6) will be left in the residue undissolved by the salicylate. The sulfide of any iron so carried down dissolves slowly, giving a deep-red color to the solution.

Procedure 42.—*Separation of Titanium from Vanadium.*—Transfer the salicylate filtrate (P. 41) to a 500-cc. casserole, and evaporate it to 40–60 cc. Cool the solution till the salicylic acid begins to separate, pour it at once into a 150–200 cc. separating funnel, and add to it gradually 6 cc. of 18 n. H_2SO_4, keeping the mixture cool with running water. Add to the cold mixture 40 cc. of ether, shake the funnel till the contents are thoroughly mixed, let it stand till the two layers separate, and draw them off separately. Return the aqueous solution to the funnel, and repeat these operations with two successive 10-cc. portions of ether.

Reject the ether solutions.

Evaporate the aqueous solution (without filtering it) in a casserole to a volume of 15–20 cc., make the solution alkaline with 6 n. NaOH, and add 10 cc. more. Boil the mixture for 3–5 minutes, and filter it. Wash the precipitate thoroughly with hot water. (White precipitate, presence of TITANIUM.)

Treat the precipitate by P. 43. Treat the solution by P. 44.

Notes.—1. The solution is concentrated by boiling, acidified, and shaken with ether, in order to remove the salicylic acid which otherwise would interfere with the later operations. The salicylic acid could be removed almost completely by precipitating it from the cold filtrate with a slight excess of H_2SO_4 and filtering it out; but this is inadmissible, since when phosphate is present the acid also precipitates much of the titanium, which does no harm if the solution be not filtered. Titanium does not pass in appreciable quantity into the ether extract containing the salicylic acid. The extraction of the salicylic acid from the acidified aqueous solution is complete after three shakings, as its distribution-ratio between ether and water is large.

2. The boiling with the NaOH solution separates vanadate and phosphate (as well as any tungstate) from the titanium and from any zirconium present. This separation is so complete that 1 mg. of vanadium in the presence of 200 mg. of titanium can be detected in the filtrate. The mixture is made 1–2 n. in NaOH, since this suffices for the decomposition, and since at higher concentrations, such as 6 n., several milligrams of titanium may dissolve.

3. A very small NaOH precipitate may arise from zirconium (see Note 1, P. 41). The confirmatory tests with H_2O_2 and Na_2HPO_4 in P. 43 distinguish titanium from zirconium, as well as from many other elements.

Procedure 43.—*Confirmation of Titanium.*—Dissolve the NaOH precipitate (P. 42) by pouring repeatedly through the filter a 5–10 cc. portion of hot 6 n. HNO_3 to which have been added 2–3 cc. of 1 f. H_2O_2. (Orange-yellow or orange-red solution, presence of TITANIUM.)

In case there is no orange color, reject the solution.

In case there is an orange color, add to the solution just 3 cc. of 6 n. H_2SO_4, and evaporate it till the H_2SO_4 begins to fume. Cool the solution, add to it 5 cc. of water and 10 cc. of 1 f. H_2O_2, and filter out any residue. Add to the filtrate 10 cc. of 1 n. Na_2HPO_4, and let it stand for half an hour. (Small white precipitate, presence of ZIRCONIUM.) Filter out any precipitate, add to the filtrate powdered Na_2SO_3, a little at a time, till it is decolorized, and let it stand at least half an hour. (White precipitate, presence of TITANIUM.)

Notes.—1. H_2O_2 is added to the HNO_3 in order to aid in dissolving the NaOH precipitate and to show the presence of titanium by the characteristic color which it produces. With 0.1 mg. of titanium the solution has a yellow color, and with larger quantities an orange-yellow to orange-red one. Vanadium, which may be present in the salicylic acid solution (see Note 3, P. 41), gives a similar color with H_2O_2; but it should have been removed by the NaOH boiling in P. 42. Even if it were still present, it would give no precipitate with Na_2HPO_4 in the subsequent test.

2. Zirconium will not be present in the NaOH precipitate in quantity larger than 1 mg. Unlike titanium, it gives even in the presence of H_2O_2 a precipitate with phosphate in acid solution. Its precipitation is practically complete in half an hour under the favorable conditions provided in the Procedure; namely, low concentration of H_2SO_4 (less than 0.7 n.) and high concentration of Na_2HPO_4. Its formula is probably $Zr(HPO_4)_2 \cdot H_2O$, but the isomeric formula $ZrO(H_2PO_4)_2$ is possible.

3. From the acid solution containing H_2O_2 even a large amount of titanium does not precipitate with the Na_2HPO_4 upon standing several hours. But, under the conditions of the Procedure, after the peroxide is reduced by the Na_2SO_3, less than 1 mg. of titanium produces a precipitate within 10–15 minutes. The completeness of the precipitation increases as the concentration of hydrogen-ion is decreased. The 3 cc. of 6 n. H_2SO_4 added would produce in the final volume (about 26 cc.) a 0.7 n. H_2SO_4, and this permits the precipitation of 1 mg. of titanium. Some acid, however, is always lost in the fuming, and any excess of Na_2SO_3 added lowers the hydrogen-ion concentration. For the reduction of the H_2O_2 Na_2SO_3 is used rather than $NaHSO_3$, since with the latter free acid would be produced by the reaction. At best, the phosphate precipitation is much less delicate than the color test with H_2O_2.

Procedure 44.—*Detection of Phosphate and of Vanadium.* —To one fifth of the NaOH filtrate (P. 42) add 6 n. HNO_3 till it is acid, heat it nearly to boiling, and pour it into a clear mixture of 5 cc. of 6 n. HNO_3 and 5 cc. of $(NH_4)_2MoO_4$ reagent, previously heated to about 60°, and let it stand for 5–15 minutes. (Yellow precipitate, presence of PHOSPHATE.)

To the remainder of the NaOH filtrate (P. 42) add 6 n. HCl till it is acid and then 3 cc. more, and saturate the solution with H_2S. (In case there is a black precipitate, heat the mix-

ture in a pressure-bottle as described in P. 37, cool, and filter out the precipitate.) Neutralize the solution with 6 n. NaOH, add to it 3 cc. of 6 n. NH_4OH, and completely saturate it with H_2S. (Violet-red solution, presence of VANADIUM.)

In case the solution is colored, pour it gradually into 15 cc. of 6 n. H_2SO_4, shaking the mixture continuously during the addition and for 1–2 minutes afterwards. (Black precipitate, presence of VANADIUM.)

Notes.—1. Since any phosphate remaining in the tantalum-group residue (in P. 30) may pass into the salicylate solution (P. 41) or may remain with zirconium in the residue, it is tested for both here and in P. 46. It has already been tested for in the tungsten group (in P. 40). Usually, however, it remains in the $HClO_4$ solution in P. 6, and is detected in P. 91.

2. As to the test for vanadium with H_2S in ammoniacal solution and the interference of molybdenum with this test, see Notes 2 and 3, P. 39. Molybdenum is not likely to be present at this point (see Note 3, P. 41); but as a precaution the acid solution is treated with H_2S; and if a precipitate results, treatment under pressure is employed to ensure complete removal of the molybdenum. Tungsten, if present, would give no color to the $(NH_4)_2S$ solution. Since ammonium salts lessen the delicacy of the H_2S test for vanadium, the HCl acid solution is neutralized with NaOH rather than with NH_4OH. Under the conditions of this Procedure 0.2 mg. of vanadium can be detected.

3. As to the precipitation of vanadium (and tungsten) as sulfide by the addition of the $(NH_4)_2S$ solution to 6 n. H_2SO_4, see Note 2, P. 31. Even though the vanadium is not completely precipitated and its precipitation is not so delicate nor characteristic as the color test, it affords a better estimate of the quantity present, except when this is small. If desired, the precipitate may be dissolved in a mixture of HCl and HNO_3, and the solution treated by the last paragraph of P. 106, in order to further confirm the presence of vanadium by precipitating it as NH_4VO_3.

Procedure 45.—*Separation of Tantalum and Columbium from Zirconium and Bismuth.*—Transfer the residue from the salicylate treatment (P. 41) to a platinum crucible, incinerating the filter in a platinum spiral. Add to the residue 1 cc.

of 27 n. HF, 1–2 cc. of 18 n. H_2SO_4, and 0.5 cc. of 16 n. HNO_3. Evaporate the mixture (see Note 7, P. 3) until dense fumes of H_2SO_4 are given off. Let it cool somewhat, add a few drops of 16 n. HNO_3, and heat it to fuming. (If organic matter is still present, repeat this treatment with HNO_3 and H_2SO_4.) Then evaporate the mixture to dryness, finally heating it over a small flame only till fumes cease to come off. (No residue, absence of TANTALUM, COLUMBIUM, ZIRCONIUM, and BISMUTH; see Note 1.) Mix the residue in the crucible with 2–5 g. of anhydrous K_2CO_3 and 0.1 g. of KNO_3, cover the crucible, heat it strongly for 5–15 minutes over a powerful burner so that complete fusion takes place. Cool the crucible suddenly by plunging its lower part while still red-hot into water. Pour into the crucible 10 cc. of cold water, stir the mixture till the melt is completely disintegrated, and pour it into a small flask. (White residue, presence of ZIRCONIUM or BISMUTH.) Filter through an HF-washed filter, and wash the residue with water.

Treat the aqueous extract by P. 46.

Treat the residue by P. 49.

Notes.—1. The treatment of the residue with HF, HNO_3, and H_2SO_4 removes silica and destroys organic matter. If nothing remains after fuming off the H_2SO_4, it shows the absence of tantalum and columbium in the substance, and of zirconium and bismuth at this point; and the fusion with K_2CO_3 and the following Procedures (P. 46–49) may then be omitted. In drawing this conclusion, however, it should be borne in mind that in the dry compact form 1 or 2 mg. of these elements make a small showing. To determine whether a small residue is significant, the crucible may be weighed, the residue dissolved in HF, the solution poured out, and the crucible heated and reweighed.

2. By the fusion with K_2CO_3 tantalum and columbium are separated from zirconium and bismuth, and from impurities (see Note 4, P. 41) that may have remained in the residue from the salicylate treatment. Thus, 2 mg. of tantalum or columbium when associated with 100 mg. of zirconium pass almost completely into the aqueous extract, and of 100 mg. of tantalum or columbium alone not more than 0.5 mg. remains in the residue; while zir-

conium always remains completely undissolved. Titanium, which should be present only in small amount, remains entirely with the zirconium, unless columbium is present, in which case some of it passes into the aqueous extract. A very little KNO_3 is mixed with the K_2CO_3, in order to avoid reduction of bismuth or lead (possibly present in small quantity), which would injure the platinum crucible.

3. The fusion is made with K_2CO_3, instead of with Na_2CO_3, because at the higher temperature at which the former melts the oxides of tantalum and columbium are taken up more quickly by the flux, and because potassium tantalate dissolves more readily in K_2CO_3 solution than the sodium salt would in a Na_2CO_3 solution. The melt is treated with only a small volume of cold water, since tantalum, and to a less extent columbium, tends to precipitate when the solution is hot or dilute. Thus 10 cc. of an aqueous extract containing 100 mg. of tantalum and 5 g. of K_2CO_3 remained perfectly clear for 24 hours, but gave a precipitate when heated, or when diluted and allowed to stand.

Procedure 46.—*Precipitation of Tantalum and Columbium and Detection of Phosphate.*—Dilute the aqueous extract from the K_2CO_3 fusion (P. 45) to 25 cc. in a flask, pass into it SO_2 gas till it smells strongly of SO_2, and heat it on a steam-bath for 30 minutes, meanwhile passing a slow current of SO_2. (White precipitate, presence of TANTALUM or COLUMBIUM.) Filter the mixture through an HF-washed filter, and wash the precipitate with hot water.

Treat the precipitate by P. 47.

To 5 cc. of the filtrate add 2 cc. of 18 n. H_2SO_4, boil the mixture till the SO_2 is expelled, pour the hot liquid into a clear mixture of 5 cc. of 6 n. HNO_3 and 5 cc. of $(NH_4)_2MoO_4$ reagent previously heated to about 60°, and let it stand 5–15 minutes. (Yellow precipitate, presence of PHOSPHATE.) Reject the mixture and the remainder of the filtrate.

Notes.—1. When the diluted K_2CO_3 solution is acidified with H_2SO_3 and then heated in its presence, the tantalum and columbium are completely precipitated within half an hour. This treatment also tends to remove tungsten, molybdenum, or vanadium, since they are not precipitated from $KHSO_3$ solution by H_2SO_3.

2. H_2SO_3 is used for the acidification, rather than HCl or H_2SO_4. For with the latter acids the precipitation of tantalum and columbium is less rapid; especially in the case of columbium, where it may not be complete even after long boiling.

3. As to the division of phosphate in the analysis of the tungsten and tantalum groups, see Note 1, P. 40, or P. 44.

Procedure 47.—*Detection of Tantalum and its Separation from Columbium.*—Dissolve the SO_2 precipitate (P. 46) by pouring a 2-cc. portion of 27 n. HF repeatedly through the filter supported in a bakelite or hard-rubber funnel, collecting the solution in a platinum crucible. Wash out the filter with 1–2 cc. of water, adding these washings to the filtrate. Add to the solution 1 cc. of 16 n. HNO_3, and evaporate the mixture just to dryness (see Note 7, P. 3). To the residue add 2 cc. of 27 n. HF and 0.5 g. (roughly weighed out) of solid K_2CO_3 (or 1.2 cc. of 6 n. K_2CO_3), evaporate the solution to dryness, and heat the residue over a small flame only till it becomes enamel-white, not allowing even the bottom of the crucible to become dull-red. Dissolve the residue in 2–3 cc. of water, boil the solution down to about 0.5 cc., add to it 4 cc. of water, and heat the solution to boiling. Pour it into a small test-tube, and allow it to stand at least 15 minutes. (Greyish-white, translucent, viscous-seeming precipitate, presence of TANTALUM.) Filter the mixture, using an HF-washed filter.

Treat the filtrate by P. 48.

Treat the precipitate again by this Procedure in case it does not have the characteristic appearance of potassium oxyfluotantalate.

Notes.—1. The evaporation of the HF solution with HNO_3 before adding the K_2CO_3 serves to volatilize any silicon which may have been taken up from the dishes and filter-paper used. The HNO_3 is added to prevent any loss of tantalum or columbium by volatilization.

2. By the addition of HF and of K_2CO_3 the tantalum is converted into K_2TaF_7 and the columbium into K_2CbOF_5. The quantity of K_2CO_3 added is much less than equivalent to the HF, so that KHF_2 is produced. The evaporation and moderate ignition expel the excess of HF. The ignition should be made at a

low temperature, as directed in the Procedure, since otherwise a large part of the columbium may be volatilized.

3. Of the compounds thus formed the K_2CbOF_5 is fairly soluble in cold water, and K_2TaF_7 slightly soluble. By the boiling with water, the tantalum compound is converted into the much less soluble oxyfluotantalate, $2K_2TaF_7 \cdot Ta_2O_5$. This separates as a heavy greyish, translucent, viscous-seeming precipitate of characteristic appearance. A quantity of tantalum as small as 1 mg. separates from the 5 cc. of solution, even while it is hot; but the test is made more delicate by cooling the mixture and letting it stand. The presence of much columbium, moreover, does not prevent the precipitation of even a small quantity of tantalum. Under the conditions of the Procedure even 100 mg. of columbium remain in solution. If it should precipitate, the K_2CbOF_5 is readily distinguished by its separation in the form of white, semitransparent, granular crystals, and by its redissolving on slightly diluting and warming the mixture.

4. Titanium or zirconium, if more than a small quantity (about 10 mg. of Ti or 25 mg. of Zr) were present here, would precipitate in the tantalum test as coarsely crystalline substances, since K_2TiF_6 or K_2ZrF_6 is not very soluble in cold water. Enough of them to interfere with this test should not reach this point, however, since titanium is removed by the previous treatment with salicylate, and both titanium and zirconium by the fusion with K_2CO_3 (see Note 2, P. 45).

5. When the precipitate has the characteristic appearance of the oxyfluotantalate, it is not necessary to treat it further. When, however, a coarsely crystalline precipitate forms, which might arise from the presence of sufficient columbium (or titanium or zirconium), the precipitate is treated again by the Procedure.

Procedure 48.—*Detection of Columbium.*—To the filtrate from the fluoride precipitate (P. 47) in a platinum crucible, add 1–2 cc. of 18 n. H_2SO_4, and evaporate the solution till the H_2SO_4 fumes strongly. Cool the mixture, and add it to 5 cc. of water in a small flask. Add 6 n. NH_4OH, 1 cc. at a time, till the mixture after shaking smells of it, and heat it to boiling. Then add, without waiting, 6 n. H_2SO_4, 1 cc. at a time, till the solution is acid, then 1 cc. more, and heat it to boiling. (White precipitate, presence of COLUMBIUM.) Collect the precipitate on a HF-washed filter, and wash it with hot water.

Dissolve the precipitate by pouring a 2-cc. portion of 27 n. HF repeatedly through the filter, and wash out the filter with 1–2 cc. of water. To the HF solution in a platinum crucible add 2 cc. of 18 n. H_2SO_4, and evaporate until the H_2SO_4 fumes strongly. Cool the mixture; add to it, drop by drop, 1 cc. of 6 n. HCl, keeping the mixture cool; introduce about 0.1 cc. of granulated Zn; and let the action continue for only 2 or 3 minutes. (Blue color, indication of COLUMBIUM.) Dilute the solution with 3 cc. of water.

Prepare a zinc reductor as follows. Place a straight drying tube, 1.5–1.7 cm. in bore, in a vertical position. Cover the opening at the bottom of the bulb with a round disk of filter-paper of about the diameter of the tube, and place on top of it a little glass-wool. Charge the tube about 6 cm. deep with finely granulated Zn which has been previously slightly amalgamated by washing it once with 0.3 n. HCl, stirring it with a solution 0.01 n. in $HgCl_2$ and 0.3 n. in HCl for only 30 seconds, pouring off the liquid, and washing with water. To the stem of the tube attach a glass tip by means of a rubber tube provided with a pinch-cock.

Pour through the reductor 2 n. HCl, and collect 10 cc. of the runnings in 5 cc. of 0.2 n. $HgCl_2$, to make sure that no turbidity results. Leave enough of the acid in the apparatus to just cover the Zn. Now pour into the tube the solution obtained as described in the second paragraph, and bring it into contact with the Zn by at once running out liquid till the solution comes nearly down to the surface of the zinc. Let the mixture stand for 5 minutes. Then place the tube so that it delivers just below the surface of a mixture of 5 cc. of 0.2 n. $HgCl_2$ and 0.5 cc. of 6 n. HCl; and let the solution run into this mixture, at the same time adding to the reductor from a graduate 10 cc. of 2 n. HCl so that the liquid is always slightly above the surface of the Zn. (Immediate white precipitate, presence of COLUMBIUM.)

Notes.—1. The H_2SO_4 solution is first treated with NH_4OH, and the mixture after heating to boiling is reacidified; for it is

a characteristic property of $HCbO_3$ and $HTaO_3$ precipitated by NH_4OH that they do not redissolve in dilute acids (other than HF). The test shows whether columbium may be present, and when negative makes unnecessary the reduction test.

2. When the Zn is first added to the undiluted solution a blue color results when columbium is present,—a pale blue with even 1–2 mg. and a dark blue with 20 mg. When the reduction is complete, as it is after the treatment in the reductor, a dark brown or dark green color results even with a fairly small quantity of columbium. Neither tantalum nor zirconium produces any coloration. Titanium gives a distinct reddish-violet color when 2 mg. are present.

3. Columbium is reduced by Zn to the trivalent state; and the resulting $CbCl_3$ at once reduces $HgCl_2$ to HgCl. Although many other substances cause this reduction (see Note 5), the columbium has been so thoroughly purified that the precipitation of HgCl at this point is a satisfactory confirmatory test. The test is sufficiently delicate to detect less than 1 mg. of columbium. The reduction may be very slow, if the Zn in the reductor has been too heavily amalgamated; the directions of the Procedure must therefore be carefully followed in this respect.

4. The following elements, if present, would not interfere with this test. Tantalum or zirconium is not reduced at all by the Zn; iron, though changed to the ferrous state, does not reduce $HgCl_2$; lead or tin is reduced to the metallic state and retained in the reductor. Titanium is reduced to the trivalent state; but the $TiCl_3$ produced reacts only very slowly with $HgCl_2$ in the cold, and even a large quantity of titanium does not give a precipitate within 10 minutes.

5. If tungsten, molybdenum, or vanadium were present in the solution poured through the zinc reductor, it would cause reduction of the $HgCl_2$; but these tungsten-group elements, in so far as they were carried down with the tantalum group in P. 30, should have been eliminated by the preceding treatments, namely by the boiling with salicylate, the precipitation by SO_2 after the fusion with K_2CO_3, and the NH_4OH precipitation at the beginning of this Procedure.

Procedure 49.—*Detection of Zirconium and Bismuth.*—Transfer the residue from the K_2CO_3 fusion (P. 45) to a platinum crucible, incinerating the filter. Add 3 g. of $K_2S_2O_7$, cover the crucible, and heat it gradually to such a temperature that its lower part is dull red. Keep it at this temperature for

5–15 minutes. Cool the crucible suddenly by placing its lower part in water, and transfer the contents to a casserole. Add 20 cc. of water, and boil the mixture till the mass is disintegrated. Cool the solution, and without filtering, saturate it with H_2S, and filter the mixture.

If there is more than a very small black precipitate, test it for BISMUTH, by dissolving it in 2 n. HNO_3, and treating the solution by P. 81–83.

Boil the filtrate from the H_2S precipitate till the H_2S is expelled, filter the solution if it is not clear, cool it, add to it 2 cc. of 1 f. H_2O_2 and 10 cc. of 1 n. Na_2HPO_4, and let it stand for an hour. (White precipitate, presence of ZIRCONIUM.)

Notes.—1. The residue of ZrO_2 from the K_2CO_3 fusion might be dissolved by continued treatment with concentrated H_2SO_4 and HF; but the fusion with $K_2S_2O_7$ is a more rapid method of bringing it into solution. Little, if any, columbium should be left with the zirconium after the K_2CO_3 fusion (see Note 2, P. 45); but even if several milligrams were present, it would give no precipitate in the zirconium test with Na_2HPO_4 in 24 hours, provided H_2O_2 is present. The solution may be faintly yellow, owing to the presence of a small amount of platinum taken up from the crucible. The residue left undissolved by the boiling water will contain in the form of sulfates all the bismuth and lead that were present in the material fused with K_2CO_3. It may also contain a little ZrO_2, Ta_2O_5, and Cb_2O_5.

2. The aqueous solution of the fusion, together with any residue, is treated with H_2S, whereby the lead and bismuth sulfates are immediately converted into sulfides. This precipitate is then filtered off and tested for bismuth in the usual way. A very small black precipitate may consist only of PtS_2 arising from the platinum taken up from the crucible. Not more than 2–5 mg. of bismuth will be found at this point because of the small solubility of BiF_3 in HF solution in P. 7; but the test should not be omitted, since in rare cases all of a small amount of bismuth present in the original material may be found here (see Note 6, P. 6).

3. As to the precipitation of $Zr(HPO_4)_2$ in a dilute acid solution by Na_2HPO_4, and the prevention of the precipitation of $Ti(HPO_4)_2$ by the addition of H_2O_2, see Notes 2 and 3, P. 43. Even if a little columbium is present, it is not precipitated under the conditions of the test.

ANALYSIS OF THE GOLD GROUP

With Nathan F. Scudder

Tabular Outline VI

Analysis of the Gold Group

Solution of Hg, Au, Pt, ‡Ir, Pd, ‡Rh as chlorides (P. 9).
Shake with ethyl acetate (P. 51).

<table>
<tr>
<td>Ester layer: $HgCl_2$, $AuCl_3$.
Shake with 3 n. NH_4Cl (P. 52).</td>
<td colspan="4">Water layer: H_2PtCl_6, H_2IrCl_6, H_2PdCl_4, H_3RhCl_6.
Add HCl, evaporate, add water and NH_4Cl (P. 55).</td>
</tr>
<tr>
<td rowspan="2">Ester layer: $AuCl_3$.
Evaporate, ignite, dissolve in HCl-HNO_3, add NaOH and KI (P. 53).</td>
<td>Water layer: $(NH_4)_2HgCl_4$.
Add NaOH and KI (P. 54).</td>
<td colspan="2">Precipitate: $(NH_4)_2PtCl_6$, $(NH_4)_2IrCl_6$.
Dissolve in HCl-HNO_3; evaporate; add water, then $NaHCO_3$ and Br_2 (P. 56).</td>
<td>Filtrate: $(NH_4)_2PdCl_4$, $(NH_4)_3RhCl_6$.
Pass in Cl_2 gas (P. 57).</td>
</tr>
<tr>
<td>Precipitate, orange: $HgO.HgINH_2$.</td>
<td>Precipitate, black: IrO_2.
Confirm iridium (P. 77).</td>
<td>Filtrate: Na_2PtCl_6.
Add HCl, evaporate, add water and NH_4Cl.</td>
<td>Precipitate, red: $(NH_4)_2PdCl_6$.</td>
<td>Filtrate, red: $(NH_4)_3RhCl_6$.
Confirm rhodium (P. 78).</td>
</tr>
<tr>
<td>Precipitate, red or purple: Au.</td>
<td></td>
<td>Precipitate, yellow: $(NH_4)_2PtCl_6$.</td>
<td></td>
<td></td>
</tr>
</table>

‡ This sign signifies that some or all of the element may be found here when it is associated with certain other elements.

General Discussion

D. 51. Isolation of the Gold Group (P. 6–9).—The gold group consists by definition of those elements which are completely precipitated as metals by boiling with formic acid (in P. 6); namely, mercury, gold, platinum, and palladium. With these elements may, however, be precipitated according to circumstances a greater or less proportion of any iridium and rhodium present (see D. 8). Iridium and rhodium must therefore be provided for in the analysis of the gold group. Moreover, since these two metals may dissolve only partially on treatment with hydrochloric and nitric acids, it is advisable to test for them also in any residue remaining after the removal of this group.

From the residue from the perchloric and formic acid treatments the tungsten and tantalum groups have already been ex-

tracted with hydrofluoric acid (see D. 9), and certain fluorides thereby produced and certain sulfates that may be originally present have been removed by boiling with sodium carbonate solution and extracting the precipitates with dilute perchloric acid (see D. 10). The gold group is thereby left as metals, associated with any of the original material that may still remain unattacked. From the latter these metals are separated by heating with hydrochloric and nitric acids. Thereby a solution of the gold group (including some or all of the iridium and rhodium) is obtained, nearly free from all other elements.

D. 52. Separation of Gold and Mercury from Other Elements and from Each Other (*P. 51–54*).—The acid solution of the gold group is evaporated and the residue is taken up with nitric acid, so as to obtain the elements in the form of chlorides in a dilute nitric acid solution. This solution is shaken twice with ethyl acetate, whereby the mercury and gold are completely extracted and the other elements left in the solution. The success of this separation depends in the case of mercury upon the absence of any considerable quantity of chloride ion; but this condition is readily attained. Ethyl acetate is used, rather than ethyl ether, since it was found to extract mercury in much larger proportion.

The mercury and gold are then separated from each other by shaking the ethyl acetate extract with 3 normal ammonium chloride. This causes the mercury to pass into the aqueous layer, owing to its tendency to form complex anions (such as $HgCl_4^=$), but removes from the ester layer not more than two percent of the gold. Gold is then tested for by evaporating the ester, dissolving the residue in a little water and acid, and precipitating the metal by adding sodium hydroxide and potassium iodide. Mercury is detected by adding these same reagents to the ammonium chloride layer, thus reversing the familiar Nessler test. The conditions for delicacy of both these tests were carefully studied.

D. 53. Separation and Detection of Platinum, Iridium, Palladium, and Rhodium (*P. 55–57*).—For the separation of the elements present in the aqueous solution (platinum, iridium, palladium, and rhodium), the well-known ammonium chloride process has been adopted. By evaporating the solution, adding 1 cc. of water, and saturating this with ammonium chloride, the platinum

and iridium (down to less than 0.5 mg.) are precipitated, while even 100 mg. of palladium or rhodium remain in solution.

The red coloration of the ammonium chloride precipitate furnishes, as experiments showed, a delicate test for the presence of iridium and a preliminary estimate of its quantity. As a means of confirming its presence when the precipitate has a distinctly reddish shade, the available methods of separating platinum and iridium were studied. The most satisfactory one was found to be that recommended by Mylius and Mazzucchelli,[1] in which the iridium is precipitated as the black dioxide by sodium hypobromite in sodium hydrocarbonate solution, and the platinum is left in the solution. This method, as adapted to the analysis of this group, consists in heating the ammonium chloroplatinate and chloroiridate with hydrochloric and nitric acids (whereby the ammonium ion is rapidly destroyed), evaporating the mixture, treating the residue with dilute sodium hydrocarbonate solution, adding a mixture of bromine and sodium hydrocarbonate, and heating. The presence of iridium in the precipitate and that of platinum in the filtrate are confirmed by precipitating these elements separately with ammonium chloride, after properly preparing the solution.

Finally, the palladium is precipitated as ammonium chloropalladate, $(NH_4)_2PdCl_6$, in the filtrate from the ammonium chloride precipitate by saturating it with chlorine. This simple process furnishes probably the most characteristic test that exists for palladium. Any rhodium that may be present remains in the filtrate, and is tested for in a way to be later described.

[1] Mylius and Mazzucchelli, *Z. anorg. Chem.*, 89, 14, 28 (1914).

ANALYSIS OF THE GOLD GROUP

Tabular Outline VI

See page 110.

Procedures and Notes

Procedure 51.—*Separation of Mercury and Gold from the Platinum Elements.*—In case the HNO_3 solution * (P. 9) is colorless, add to one fifth of it in a test-tube two drops of 1 n. $SnCl_2$, and let it stand 1–2 minutes. (Grey or black precipitate, or purple, orange, or dark color, presence of GOLD GROUP.) Reject the mixture.

In case the HNO_3 solution is colored, or in case it is colorless and the $SnCl_2$ test with the small portion has given a positive result, add to it one drop of 6 n. HCl, and shake the solution vigorously for a minute in a small short-stem separating funnel (see Note 4) with 10 cc. of pure ethyl acetate. Draw off the aqueous layer, and shake it with a fresh 10-cc. portion of ethyl acetate.

Treat the first and second ethyl acetate extracts separately by P. 52, to detect mercury and gold.

Treat the aqueous solution by P. 55, to detect platinum, iridium, palladium, and rhodium.

Notes.—1. The diluted HNO_3 solution of the gold group is yellow or dark-orange when it contains even a few milligrams of gold, platinum, palladium, iridium, or rhodium. Since, however, a solution may contain a smaller quantity of these elements or a large quantity of mercury without showing color, a portion of it is in this case tested with $SnCl_2$ to determine whether any gold-group element is present. When this reagent is added to 2 cc. of solution even 0.1 mg. of any of the gold-group elements gives either a noticeable precipitate or color; thus 0.1 mg. of gold gives a

* For practice-analyses use a solution made by evaporating a mixture of test-solutions of mercury, gold, platinum, iridium, and palladium (1 cc. of each) with 3 cc. of 16 n. HNO_3 to a volume of 0.5–1.0 cc. and diluting with 12 cc. of water.

violet color; of mercury, a grey precipitate; of platinum, an orange-yellow color; and of palladium, a dark-orange color.

2. Since the solution containing the gold group was previously (in P. 9) evaporated to a small volume with excess of HNO_3, it contains no chloride except that which is combined with the gold-group elements. This is essential, since mercury is not extracted by ethyl acetate when the aqueous solution contains much chloride (because this converts $HgCl_2$ into $HgCl_4^=$). A drop of 6 n. HCl is added to make sure that the mercury and gold are wholly in the form of their chlorides.

3. Under the conditions of the Procedure the ethyl acetate extracts scarcely any of the platinum, iridium, palladium, or rhodium (not enough to give the ester layer a yellow color); but it removes nearly all of the gold and mercury (thus in one shaking all but 0.5 mg. of gold out of 30 mg., and all but 1–2 mg. of mercury out of 100 mg.). The chloride concentration has little influence on the distribution of the gold; but, as stated above, it must be very small in order that the mercury may be satisfactorily extracted. A small concentration of hydrogen-ion is necessary in the case of gold (probably to prevent the hydrolysis of its chloride); but beyond this, its concentration has little influence upon the extraction of either gold or mercury.

4. In order to attain a sharp separation of the two layers, it is desirable to use a separating funnel with a stem only about 1 cm. long ground at an angle of 45°. This enables the stem below the stop-cock to be washed out with a stream from a wash-bottle after the aqueous layer has been drawn off. It is also well, after nearly all the aqueous layer has been drawn off, to let the portion of it which wets the wall of the funnel drain down and then to draw off the last few drops. Since two extractions are made, it is convenient to have two such funnels available.

Procedure 52.—*Separation of Gold from Mercury.*—To the second ethyl acetate extract (P. 51) in a separating funnel add 8 cc. of 3 n. NH_4Cl, and shake the mixture vigorously for about a minute. Let the layers separate, and draw off the aqueous layer. Shake this aqueous layer with the first ethyl acetate extract (P. 51), and separate the two layers. Unite the two ethyl acetate solutions, wash the mixture by shaking it with an 8-cc. portion of 3 n. HCl, and draw off and reject the aqueous layer. (Yellow ethyl acetate layer, presence of GOLD.)

Treat the ester solution, even if it is colorless, by P. 53.

Treat the NH_4Cl solution by P. 54; first washing it, in case the ethyl acetate layer was yellow, by shaking it with 5 cc. of fresh ethyl acetate to which 3 drops of 6 n. HCl are added.

Notes.—1. Almost all the mercury (all but 1 or 2%) is removed from the ethyl acetate solution by a single shaking with 3 n. NH_4Cl, owing to the formation of the complex ion $HgCl_4^=$. On the other hand, not more than 2% of the gold is removed from the ethyl acetate by this treatment. The two ethyl acetate solutions are not united at the start, but they are shaken with 3 n. NH_4Cl successively (the one more dilute in mercury first), since thereby, in accordance with the distribution law, the mercury passes into the aqueous layer more completely. The ethyl acetate solution is washed with 3 n. HCl to remove the remainder of the mercury and any adhering NH_4Cl solution, since the simultaneous presence of these substances would give rise to a precipitate in the subsequent test for gold (in P. 53).

2. NH_4Cl is used rather than HCl in the extraction for the reasons that the aqueous solution is then ready for the precipitation of mercury in P. 54, and that ethyl acetate is much less soluble in a solution of NH_4Cl than in one of HCl.

3. A noticeable yellow color is given to 20 cc. of ethyl acetate by 3 mg. of gold; but, as the color is scarcely noticeable with a smaller quantity, the ethyl acetate layer, even if colorless, should be tested for gold by P. 53.

4. If because of mechanical inclusion some platinum has passed into the NH_4Cl solution, a yellow crystalline precipitate of $(NH_4)_2PtCl_6$ may be formed. If this occurs, the precipitate should be filtered out; platinum then causes no interference with the subsequent test for mercury with NaOH and KI.

Procedure 53.—*Detection of Gold.*—Evaporate the ethyl acetate solution (P. 52) in a small casserole to dryness on a steam-bath, heat the whole casserole to a barely visible red-heat, and cool it. To the residue add 1 cc. of 12 n. HCl and 3 or 4 drops of 16 n. HNO_3, and evaporate the mixture to a few drops. Add 5 cc. of water, 2 cc. of 6 n. NaOH, and 0.5 cc. of 1 n. KI, and heat the mixture to boiling. (Purple color or red precipitate, presence of GOLD.) If there is much precipitate, add 1 cc. more of 1 n. KI, and heat again to boiling. Treat the mixture no further.

Notes.—1. The residue is gently ignited after evaporating off the ethyl acetate to remove any mercury and ammonium salts, since these if present together would interfere with the subsequent test for gold. Too strong ignition is avoided, however, since the gold may form on the casserole a mirror which is not readily dissolved by the HCl and HNO_3.

2. Upon addition of NaOH and KI metallic Au is precipitated, slowly in the cold, rapidly on heating, as a fine red powder. With a small amount of gold a purple color results, which is noticeable with 0.2 mg. of gold. The test is not interfered with by other elements of the gold group (except by mercury in the presence of ammonium salts). It is most delicate when not more than 0.5 cc. of 1 n. KI is present, and when an excess of not less than 1 cc. of 6 n. NaOH has been added.

Procedure 54.—*Detection of Mercury.*—To the NH_4Cl solution (P. 52) add an equal volume of 6 n. NaOH and 0.5 cc. of 1 n. KI. If there is no precipitate, warm the mixture, and let it stand for 5 minutes; if there is much precipitate, add 1–2 cc. more of 1 n. KI. (Orange precipitate or yellow turbidity, presence of MERCURY.)

Notes.—1. Enough 6 n. NaOH is added to metathesize all the ammonium salts and furnish a moderate excess, since this increases the delicacy of the test. A large quantity of KI decreases its sensitiveness; hence only 0.5 cc. of 1 n. KI is added at first, in which case a precipitate results with even 0.1 mg. of mercury; but, when much mercury is present, more KI is added to complete the precipitation. With 5 mg. or more of mercury a red precipitate is produced; but, when less is present, a yellowish-white cloudiness results, which changes to a flocculent precipitate after heating a short time. The precipitate has the formula $HgO \cdot HgINH_2$.

2. Gold, when present in the NH_4Cl solution in quantity of 2–4 mg., produces a light-brown turbidity, which would obscure the test for a small quantity of mercury. To guard against its presence the NH_4Cl solution is washed with fresh ethyl acetate (in P. 52) when much gold is present, before adding NaOH and KI.

3. Though this final test is delicate enough to show less than 0.1 mg. of mercury, yet, owing to loss by volatilization (Note 10, P. 5, and Note 3, P. 9) and to its compactness in the metallic form (Note 11, P. 6), mercury may not be detected when less than 1 mg. of it is present in the original material.

Procedure 55.—*Separation of Platinum and Iridium from Palladium and Rhodium.*—To the aqueous solution (P. 51) add 5 cc. of 12 n. HCl, and evaporate it almost to dryness. Add 1 cc. of water, and evaporate the solution on a steam-bath till the residue no longer smells of acid. (Colorless residue, absence of PLATINUM, IRIDIUM, PALLADIUM, and RHODIUM.)

In case the residue is colorless, treat it no further.

In case the residue is colored, add to it 2 drops of 6 n. HCl, and transfer it to a small weighing bottle with the aid of not more than 1.0 cc. of water; then add powdered NH_4Cl with constant stirring or shaking till no more of it dissolves (avoiding much excess); cool the mixture, preferably in ice water, and let it stand for at least half an hour. Redissolve, if necessary, the excess of NH_4Cl by very slight warming. (Yellow crystalline precipitate, presence of PLATINUM; black precipitate, presence of IRIDIUM; red precipitate, presence of PLATINUM and IRIDIUM.) Filter the mixture through a very small filter, and wash the filter with 2–4 cc. of cold saturated NH_4Cl solution, collecting the filtrate and the first 1 cc. of wash-water in a small weighing bottle.

Treat the precipitate, in case it is red or black, by P. 56; treat it no further in case it is pure yellow.

Treat the filtrate by P. 57.

Notes.—1. The solution is evaporated first with HCl and then with water to destroy HNO_3 and any $(NO)_2PtCl_6$ (nitrosyl chloroplatinate) that may have been formed, since this prevents the complete precipitation of platinum by NH_4Cl. The evaporation also serves to reduce completely to the bivalent (palladous) state any palladium that may have been oxidized to H_2PdCl_6 by the HNO_3 and HCl. The final evaporation is made on a steam-bath so as to avoid the separation of metallic Pd. If Pd has so separated as a result of overheating, it should be redissolved by adding to the mixture 0.5 cc. of 6 n. HCl, saturating it with Cl_2, and evaporating more carefully than before.

2. If the residue is colorless, it shows the absence in it of platinum, iridium, palladium, and rhodium, in quantity as large as 0.2 mg.

3. That the NH_4Cl test for platinum and iridium may be delicate the solution must have a small volume, be saturated with NH_4Cl, be cooled, preferably in iced water, and be allowed to stand. Under the conditions of the Procedure, there results a precipitate consisting of small yellow crystals when 0.3 mg. of platinum is present, and one consisting of a dense black powder when 0.5 mg. of iridium is present; moreover, even 100 mg. of platinum are so completely precipitated that not more than 0.5 mg. remains in solution.

4. When even a small proportion of iridium is present with platinum the color of the precipitate is orange to dark-red (instead of pure yellow); thus when iridium and platinum are present in the ratio 1 : 100, the precipitate has an orange color redder than that of powdered $K_2Cr_2O_7$, and when in the ratio of 1 : 10, the precipitate has a red color darker than that of $(NH_4)_2PdCl_6$ (precipitated as in P. 57). The proportion of iridium can therefore be estimated from the color of the precipitate.

5. In case the precipitate is not pure yellow, it is treated by P. 56 in order to isolate the iridium. It should be noted, however, that the iridium usually passes mainly, and may pass wholly, into the $HClO_4$ filtrate after the boiling with $HCHO_2$ in P. 6 (see Note 9, P. 6).

6. The separation of platinum from bivalent palladium with NH_4Cl is satisfactory; thus with 100 mg. of palladium there is no precipitate, and with a mixture of 1 mg. of palladium and 100 mg. of platinum, less than half of the palladium is retained in the precipitate after washing it with NH_4Cl solution.

Procedure 56.—*Separation of Platinum from Iridium.*—Heat the NH_4Cl precipitate (P. 55) in a covered casserole with 10–20 cc. of 12 n. HCl and 0.5–1.0 cc. of 16 n. HNO_3 at 80–90° for 15–30 minutes, adding from time to time (when free Cl_2 is no longer present) 0.5 cc. more 16 n. HNO_3. Then evaporate the mixture, finally on a steam-bath, till the residue no longer smells of acid. Add 5 cc. of water and 2 cc. of 1 f. $NaHCO_3$. (Test the mixture with red litmus-paper; and, if it does not turn the paper blue, add 1 f. $NaHCO_3$, 0.5 cc. at a time, till it does so.) Heat the mixture 5 minutes on a steam-bath. Cool it somewhat, add a mixture of 1 cc. of saturated Br_2 solution with 0.5 cc. of 1 f. $NaHCO_3$; and heat the liquid on the steam-bath 5–10 minutes longer. (Blue color changing

to black precipitate, presence of IRIDIUM.) If the precipitate is large or fails to coagulate, repeat the treatment described in the last sentence. Filter the mixture, and wash the precipitate.

Acidify the filtrate with HCl, and evaporate it to dryness, finally on a steam-bath. If the residue is colorless, reject it; if it is colored, treat it by the third paragraph of P. 55. (Yellow or orange precipitate, presence of PLATINUM.)

Treat the NaBrO precipitate by P. 77, to confirm the presence of iridium.

Notes.—1. This separation of platinum from iridium with NaBrO is not satisfactory in the presence of ammonium salts. The NH_4Cl precipitate is therefore first heated with HCl and HNO_3 to destroy by oxidation the ammonium ion. This destruction takes place under the conditions of the Procedure fairly rapidly; thus it is complete within 15–30 minutes when 50 mg. of NH_4Cl or 200 mg. of $(NH_4)_2PtCl_6$ are present.

2. The separation of the platinum from the iridium is made in a slightly alkaline solution, since free acid prevents the precipitation of iridium, and since much alkali may cause platinum to be thrown down. The right hydrogen-ion concentration is attained by evaporating off the free acid and adding a small quantity of $NaHCO_3$. The mixture is then heated, since otherwise the iridium is incompletely precipitated when the NaBrO is added. Some iridium, when much is present, may be precipitated upon heating the $NaHCO_3$ solution alone; but it is not completely precipitated until it is fully oxidized to the quadrivalent state by the NaBrO. The mixture is heated so as to coagulate the precipitate; this being especially necessary when much platinum or much iridium is present. For further discussion of the precipitation of iridium by NaBrO see Notes 3 and 4, P. 76.

3. Under these conditions even 0.5 mg. of iridium yields at first a blue color and on heating a flocculent black precipitate; while even 100 mg. of platinum give at most a yellow turbidity corresponding to 1–2 mg. of platinum. With a mixture of only 0.5 mg. of iridium with 100 mg. of platinum a dark flocculent precipitate results.

4. Rhodium and palladium, if they were present in the solution, would also give dark precipitates with NaBrO. The confirmatory test for iridium (in P. 77) with NH_4Cl serves to distinguish it from these elements.

Procedure 57.—*Precipitation of Palladium and Separation from Rhodium.*—Saturate the filtrate from the NH_4Cl precipitate (P. 55) with Cl_2 gas, stopper the bottle, and let it stand 30 minutes. (Red precipitate, presence of PALLADIUM.) Filter the mixture through a very small filter.

Treat the precipitate no further.

Boil the filtrate till the Cl_2 is expelled. (Red or orange color, presence of RHODIUM.) If the solution is colorless, reject it; if it is red or orange, treat it by P. 78, to confirm the presence of rhodium.

Notes.—1. The solution is saturated with Cl_2 in a bottle, and this is then stoppered, since H_2PdCl_6 undergoes spontaneous decomposition with formation of Cl_2. The test is delicate enough to show 0.5 mg. of palladium provided the volume does not exceed 2 cc., and provided the solution is saturated with NH_4Cl and with Cl_2, and is allowed to stand in the cold.

2. Since rhodium may be precipitated with the gold group in the $HCHO_2$ treatment (see Note 9, P. 6), it may be found in the filtrate from this NH_4Cl precipitate. The presence of even 1 mg. produces a red or orange color; hence the filtrate is tested for rhodium only in case it has a reddish color.

ANALYSIS OF THE THALLIUM GROUP

With Nathan F. Scudder

Tabular Outline VII

ANALYSIS OF THE THALLIUM GROUP

FILTRATE FROM THE PERCHLORIC AND FORMIC ACID PRECIPITATE (P. 6).
Add HBr, filter, wash with 1 n. HBr (P. 61).

<table>
<tr><td colspan="3">Precipitate: AgBr, TlBr, *$PbBr_2$.
Extract with boiling water and Br_2 solution (P. 62).</td><td rowspan="2">Filtrate.
Treat by P. 70.</td></tr>
<tr><td>Residue: AgBr.
Add NH_4OH (P. 62).</td><td colspan="2">Solution: $TlBr_3$, $PbBr_2$.
Add H_2SO_4 (P. 63).</td></tr>
<tr><td rowspan="2">Solution: $Ag(NH_3)_2Br$.
Add HNO_3 (P. 62).</td><td>Precipitate: $PbSO_4$.
Dissolve in NH_4-$C_2H_3O_2$, add K_2CrO_4 (P. 63).</td><td>Filtrate: $Tl_2(SO_4)_3$.
Add H_2SO_3 and KI (P. 63).</td><td rowspan="2"></td></tr>
<tr><td>Precipitate, light-yellow: AgBr.</td><td>Precipitate, yellow: $PbCrO_4$.</td><td>Precipitate, yellow: TlI.</td></tr>
</table>

* This sign shows that a large part, but not all, of the element is found here when a large quantity is present.

General Discussion

D. 61. Precipitation and Analysis of the Thallium Group (P. 61).—Before treating the main perchloric acid solution with hydrogen sulfide, it is desirable to remove those elements which can be precipitated by a halogen acid. This is done in this scheme of analysis by adding bromine-free hydrobromic acid to the cold undiluted solution. This has the advantage over hydrochloric acid that thallium, as well as silver, is completely precipitated. Any lead in excess of 15–20 mg. is also thrown down. These three elements constitute what is here called the *thallium group.* With them may be precipitated some bismuth when it is present in very large quantity; but this is returned to the solution by washing the precipitate with 1 normal hydrobromic acid solution.

The methods adopted for the separation and detection of the elements of thallium group require no special discussion. They are clearly shown in the Tabular Outline.

ANALYSIS OF THE THALLIUM GROUP

Tabular Outline VII

See page 121.

Procedures and Notes

Procedure 61.—*Precipitation of the Thallium Group.*—To the 10–12 cc. of the cold $HClO_4$ solution * (P. 6) add 2–4 cc. of 2 n. bromine-free HBr (see Note 2), and shake it frequently for at least 5 minutes. (Precipitate, presence of SILVER, THALLIUM, LEAD, or much BISMUTH; no precipitate, absence of SILVER and THALLIUM.) Filter the mixture through a small filter, and wash the residue carefully with a small quantity (5–10 cc.) of cold 1 n. bromine-free HBr, adding these washings to the filtrate.

Treat the precipitate by P. 62. Treat the filtrate by P. 70.

Notes.—1. By the action of the Br_2 used in P. 2 thallium is oxidized to the trivalent state; and it remains in this state, in the form of $Tl(ClO_4)_3$, during the fuming with $HClO_4$. The boiling with $HCHO_2$ in P. 6 reduces it completely to $TlClO_4$. An excess of HBr is added to the cold solution (previously evaporated to 10–12 cc.), and the mixture is shaken from time to time, so as to make the precipitation of thallium as complete as possible; for the solubility of TlBr in water is not inconsiderable.

2. Since commercial HBr usually contains free Br_2 and this oxidizes a corresponding quantity of thallium and prevents its precipitation, it is essential to use a bromine-free reagent. This may be prepared when needed by adding to 9 n. HBr an equal volume of 12 n. $HCHO_2$ and 2½ volumes of water, and heating the mixture almost to boiling for a few minutes. The acid is diluted to 2 n., since the reaction between Br_2 and $HCHO_2$ is very slow in a solution much more strongly acid. In place of the HBr 2 n. NH_4Br may be used; but this may cause the precipitation of NH_4ClO_4, especially when the liquid contains more $HClO_4$ than usual, or of yellow ammonium phosphomolybdate when molybdenum and phosphate are both present.

* For practice-analyses use a mixture of 1 cc. of silver test-solution, 1 cc. of thallous test-solution, 5 cc. of lead test-solution, and 3 cc. of 9 n. $HClO_4$.

3. When the directions are followed a precipitate results with less than ½ mg. of thallium; and 100 mg. of thallium are thrown down as a light-yellow curdy precipitate to such an extent that not more than ½ mg. remains in solution. The HBr also precipitates all the silver as pale yellow AgBr, any lead present in excess of about 15 mg. as white $PbBr_2$, and any bismuth present in excess of about 250 mg. as light-yellow $BiBr_3$.

4. Since TlBr is somewhat soluble in water, the precipitate is washed with as small a quantity of cold bromine-free HBr solution as will free it completely from adhering liquid. This washing also dissolves precipitated $BiBr_3$, 10 cc. sufficing to dissolve nearly all the bismuth even when 500 mg. were originally present. The washings are added to the filtrate so that no considerable quantity of lead or bismuth may be lost.

Procedure 62.—*Separation of Thallium and Lead from Silver, and Detection of Silver.*—Through the filter containing the HBr precipitate (P. 61) pour repeatedly a 15-cc. portion of boiling water, and then repeatedly a 15-cc. portion of saturated Br_2 solution. Wash the residue with boiling water, rejecting these washings. (Yellow residue, presence of SILVER.)

Transfer the residue undissolved by hot water and Br_2 solution with the filter to a casserole, pour over it 5–10 cc. of 15 n. NH_4OH, warm the mixture to 40–50° for 5 minutes with occasional stirring, and filter it. Boil the filtrate down to half its volume, make it acid with 6 n. HNO_3, and add a few drops of 2 n. HBr. (Yellow precipitate, presence of SILVER.) Treat the precipitate no further.

Unite the hot-water and Br_2-solution extracts, evaporate the mixture to about 10 cc., and treat it by P. 63.

Notes.—1. The hot-water treatment extracts some thallium, and all the lead when not more than 200–300 mg. of it is present. The treatment with Br_2 solution extracts the rest of the thallium, owing to the conversion of TlBr into readily soluble $TlBr_3$. The final washing separates any lead still remaining on the filter from the AgBr, of which an appreciable quantity is not dissolved by these treatments. Any bismuth present in the precipitate remains undissolved as white BiOBr with the AgBr. It may pass through the filter as a turbidity at first, and in that case must be removed by filtration, repeated if necessary.

2. Though AgBr is much less soluble in NH_4OH than AgCl, yet 10 cc. of 15 n. NH_4OH, when used as directed in the Procedure, bring into solution about 100 mg. of silver. This gradually separates out as the NH_3 is boiled out of the filtrate.

Procedure 63.—*Detection of Lead and Thallium.*—To the extracts (P. 62) from the HBr precipitate add 2 cc. of 6 n. H_2SO_4. (White precipitate, presence of LEAD.) Filter, and wash the precipitate with 2 n. H_2SO_4, then with a little water.

Pour repeatedly through the filter containing the H_2SO_4 precipitate a 5–15 cc. portion of 3 n. $NH_4C_2H_3O_2$. To the filtrate add 2–5 drops of 3 n. K_2CrO_4 and one third its volume of 6 n. $HC_2H_3O_2$. (Yellow precipitate, presence of LEAD.)

To the filtrate from the H_2SO_4 precipitate add powdered Na_2SO_3, a little at a time, till the solution smells of SO_2, then 1–2 cc. of 1 n. KI, and let the mixture stand 5 minutes. (Yellow precipitate, presence of THALLIUM.)

Notes.—1. Non-formation of a precipitate with H_2SO_4 does not show the absence of lead, since lead up to about 15 mg. passes into the filtrate from the HBr precipitate (in P. 61). Formation of a precipitate with H_2SO_4 must not be regarded as proof of the presence of lead, owing to the fact that the HBr precipitate may have retained alkaline-earth elements because of incomplete washing. The confirmatory test with K_2CrO_4 should therefore be applied to the precipitate. $BaSO_4$, unlike $PbSO_4$, does not dissolve in $NH_4C_2H_3O_2$ solution; and $SrSO_4$ or $CaSO_4$, though somewhat dissolved by this solvent, give no precipitate with K_2CrO_4 in the presence of $HC_2H_3O_2$.

2. The thallium is present in the thallic state in the filtrate from the H_2SO_4 precipitate; but it is immediately reduced by H_2SO_3, even in the cold. The test with KI is sufficiently delicate to show the presence of 0.1–0.2 mg. of thallium in the solution. And the presence in the original material of 0.5 mg. of thallium alone, or of 1 mg. with 500 mg. of lead, may be detected. The appearance of a yellow or orange color in the solution when KI is added does not indicate thallium; for H_2SO_3 imparts a yellow color to KI solution.—As to the detection of thallium in a special case see Note 5, P. 94.

3. If bismuth is present in the HBr precipitate, which may be the case when large amounts of it are present, the first drop of KI may form a black precipitate of BiI_3; but this dissolves when more KI is added, giving the solution an orange color.

ANALYSIS OF TELLURIUM AND COPPER GROUPS

With G. Victor Sammet and Robert H. Dalton

Tabular Outline VIII

See page 126.

General Discussion

Acknowledgment.—A scheme of analysis for these groups, including their separation (by the silver-precipitation process described in D. 19) from the gold group (which was then present in the hydrogen sulfide precipitate because formic acid was not used in P. 6) was originally worked out by G. Victor Sammet, Ralph C. Robinson, and George H. Buchanan. The separation of iridium and rhodium from the copper group and from each other was later brought into its present improved form by Robert H. Dalton.

D. 71. Elements Precipitated by Hydrogen Sulfide from the Acid Solution.—The next step in the system of analysis is the precipitation of those elements which are thrown down from acid solution by hydrogen sulfide. The number of elements passing into this precipitate is greatly reduced by the fact that many that would otherwise be found here have been wholly or almost wholly removed by previous operations. Thus there has been eliminated substantially all of the selenium, arsenic, germanium, osmium, ruthenium, antimony, tin, mercury, gold, platinum, palladium, and silver. Moreover, any molybdenum in excess of 3 mg. (except when phosphate is also present), and any lead in excess of 20–30 mg. have been removed. Hence there will be found in the hydrogen sulfide precipitate only tellurium, molybdenum, iridium, and rhodium (constituting the *tellurium group*), and lead, bismuth, copper, and cadmium (constituting the *copper group*).

The fact that only this relatively small number of elements is precipitated by hydrogen sulfide has great advantages, first, in the respect that it much simplifies the (otherwise very complex) scheme of analysis for the precipitated elements; and secondly, in the respect that the separation of these from the elements that normally are not precipitated by hydrogen sulfide is on the average much more perfect. This last is especially important in view of the many cases[1] in which more soluble sulfides are carried

[1] See especially the recent paper by Feigl, *Z. anal. Chem.*, 65, 25–46 (1924).

Tabular Outline VIII

Analysis of tellurium and copper groups

Precipitate of Te, Mo, Ir, Rh, Pb, Bi, Cu, Cd, as sulfides (P. 71).
Dissolve in HCl and HNO_3; evaporate, add HCl, pass in SO_2 (P. 72).

- **Precipitate, black: Te.**
- **Filtrate.** *Evaporate, add 6 n. HCl, shake with ether (P. 73).*
  - **Ether layer: $MoO_3 2HCl$.** *Evaporate (P. 74).*
    - **Residue, blue: $Mo_2O_5 \cdot xMoO_3$.** *Add HCl, KSCN, Zn.*
    - **Red color: $MoO(SCN)_3$.** *Pass in H_2S.*
    - **Precipitate, brown: MoS_{2-3}.**
  - **Water layer.** *Evaporate, add water, $HC_2H_3O_2$, $NaNO_2$, and NaOH (P. 75).*
    - **Filtrate: $Na_3Ir(NO_2)_6$, $Na_3Rh(NO_2)_6$.** *Add HCl, evaporate, add Na_2CO_3 and Br_2 (P. 76).*
      - **Precipitate: IrO_2, RhO_2.** *Dissolve in HBr, evaporate with HCl and HNO_3, add water and NH_4Cl (P. 77).*
        - **Precipitate, black: $(NH_4)_2IrCl_6$.**
        - **Filtrate: $(NH_4)_3RhCl_6$.** *Add NH_4OH, evaporate, add HCl (P. 78).*
          - **Precipitate, yellow: $RhCl(NH_3)_5Cl_2$.**
      - **Filtrate: Na salts.** *Reject.*
    - **Precipitate: Pb, Bi, Cu, Cd, as hydroxides.** *Dissolve in HNO_3, add H_2SO_4, evaporate, dilute (P. 81).*
      - **Precipitate: $PbSO_4$.** *Dissolve in $NH_4C_2H_3O_2$, add K_2CrO_4 (P. 63).*
        - **Precipitate, yellow: $PbCrO_4$.**
      - **Filtrate: Bi, Cu, Cd, as sulfates.** *Add NH_4OH (P. 82).*
        - **Precipitate: $Bi(OH)_3$.** *Add Na_2SnO_2 (P. 83).*
          - **Precipitate, black: Bi.**
        - **Filtrate: $Cd(NH_3)_4SO_4$, $Cu(NH_3)_4SO_4$ (blue).**
          - *To a part add $HC_2H_3O_2$ and $K_4Fe(CN)_6$ (P. 84.)*
            - **Precipitate, red: $Cu_2Fe(CN)_6$; white: $Cd_2Fe(CN)_6$.**
          - *To the remainder add KCN (P. 85).*
            - **Solution: $K_2Cu(CN)_3$, $K_2Cd(CN)_4$.** *Pass in H_2S (P. 85).*
              - **Precipitate, yellow: CdS.**
              - **Solution: $K_2Cu(CN)_3$.**

down by less soluble ones. Moreover, the smaller number of elements to be detected makes it unnecessary to employ the very unsatisfactory separation with ammonium or sodium sulfide.

D. 72. The Hydrogen Sulfide Precipitation (P. 70–71).—The problem here presented consisted in determining the conditions under which the various elements of the tellurium and copper groups can be most rapidly and completely precipitated by hydrogen sulfide, while at the same time retaining in solution the elements of the later groups. The features not involved in common-element analysis are the difficulty of completely precipitating iridium, and in less degree much molybdenum, and the fact that indium is likely to be carried down in the sulfide precipitate.

The process finally adopted consists: (1) in treating with hydrogen sulfide at 90–100° a solution which has a volume of 30 cc., an acid concentration of 1 normal, and contains chloride; (2) in diluting the solution to 100 cc., thereby making the acid 0.3 normal, and saturating it with hydrogen sulfide in the cold; and (3), in case iridium is to be tested for or molybdenum may be still unprecipitated, filtering the mixture, evaporating the filtrate to a small volume, making it strongly acid with hydrochloric acid, saturating it cold with hydrogen sulfide, and heating it at 100° in a pressure-bottle for half an hour (or longer if iridium is slowly precipitating). This process is convenient in execution; and it gives, so far as known, an entirely satisfactory separation, except in the one respect that, even after the heating under pressure, a small portion of the iridium may remain in solution.

The conditions prevailing in the first step of the process lead to a fairly complete precipitation of all the elements of the tellurium and copper groups (except iridium) from a solution which is still so acid that there is little tendency for other elements (such as indium, zinc, nickel, and cobalt) to be carried down with them. In the second step, in which the solution is cooled and diluted so that the acid becomes only 0.3 normal, the small proportions of lead, cadmium, and bismuth that may not have been previously precipitated are thrown down. As the complete precipitation of these elements and the non-precipitation of those of the following groups is dependent on a fairly close attainment of the acid concentration 0.3 normal, the acid-content of the solution is adjusted in advance with the aid of the indicator

methyl violet by means of a simple procedure, which was worked out in detail. In the third step of the process (which has to be resorted to only rarely), the addition to the solution of concentrated hydrochloric acid and the treatment with hydrogen sulfide at 100° under pressure greatly promote the separation of iridium, which from a perchloric acid solution or from a cold hydrochloric acid solution is only very slowly precipitated. The employment of the high temperature and of hydrogen sulfide under pressure also precipitates any molybdenum still in solution.

D. 73. Separation of Tellurium and Molybdenum from the Other Elements (P. 72–73).—The solution of the sulfide precipitate is evaporated and made 3 normal in hydrochloric acid, and the tellurium is precipitated by saturating it with sulfur dioxide and heating. The only other element (aside from gold and palladium, which can not escape precipitation in the boiling with formic acid in P. 6) that would be thrown down under these conditions is selenium, and its presence is guarded against by previously passing sulfur dioxide into the solution while it is 12 normal in hydrochloric acid, whereby selenium, but not tellurium, is precipitated.

The molybdenum is then extracted with ether after reducing the volume and making the hydrochloric acid 6 normal. This method of separating molybdenum from other elements has been described by Blair.[1] It was found to be fairly effective, especially when, as in this case, the quantity to be removed is not large. Thus about 85 percent of the molybdenum passes into the ether layer when 15 cc. of this solvent are shaken with 5 cc. of the acid solution. The tellurium must be previously removed, as directed, since it also passes into ether in considerable quantity. Iridium, rhodium, and copper-group elements are not detectable in the ether layer after it has been washed with a little acid.

D. 74. Separation of Iridium and Rhodium from the Copper Group and from Each Other (P. 75–77).—The most difficult problem met with in developing the analysis of these groups was the separation of iridium and rhodium from the copper-group elements. This may be done by boiling the solution with formate, as described by Mylius and Dietz.[2] But the process requires many

[1] Blair, *J. Am. Chem. Soc.*, 30, 1229 (1908).
[2] Mylius and Dietz, *Ber. deutsch. chem. Ges.*, 31, 3191 (1898).

hours for its completion (see D. 18), and it yields the iridium and rhodium in the state of the metals, which can be brought into solution only by fusion. The most simple and effective method for this separation seems to be to convert these elements into their complex nitrites, as recommended by Leidié.[1] In this form they are not precipitated by sodium hydroxide, but this reagent precipitates the copper group. Even this process required investigation as to its details; but in the final form it gives a fairly sharp separation. The complex nitrites are first produced by making the solution slightly acid with acetic acid, adding sodium nitrite, and warming. The copper group is then precipitated with sodium hydroxide, and the precipitate is filtered out. Sodium hydrocarbonate is added to the filtrate, to destroy the excess of hydroxide, which may have caused a little lead to dissolve.

The complex nitrites of iridium and rhodium are decomposed by evaporating the solution with hydrochloric acid; but this leaves them mixed with a large quantity of sodium salts, from which they must be removed before they can be satisfactorily separated from each other. For this purpose hydrogen sulfide was at first used; but this is unsuitable because of the extreme slowness with which iridium is precipitated even when heated with the gas under pressure. Recourse was therefore had to the hypobromite method of Mylius and Mazzucchelli,[2] consisting in precipitating the dioxides of iridium and rhodium, which has already been employed in the gold group for separating iridium from platinum (see D. 53). The two dioxides are thrown out merely by heating with sodium carbonate and bromine. The only defects in the process are that, when the elements are present in large quantity, the heating must be continued with occasional addition of bromine for about an hour, and that even then a small proportion of the iridium may escape precipitation.

The dioxides of iridium and rhodium are dissolved in hydrobromic acid, the bromine displaced by chlorine by evaporating with hydrochloric and nitric acids, and the iridium precipitated with ammonium chloride. In order to detect a small quantity of iridium, it was found that special precautions must be observed; but, when this is done, the test is a very delicate one.

1 Leidié, *Bull. soc. chim.*, (3), **25**, 10 (1901).
2 Mylius and Mazzucchelli, *Z. anorg. Chem.*, **89**, 14, 28 (1914).

The rhodium is found in the filtrate from the ammonium chloride precipitate. Its presence, when indicated by the red color of the solution, is confirmed by its conversion, through heating the solution with ammonium hydroxide, into the characteristic chloropentammino-rhodium chloride, which separates from hydrochloric acid solution as a light-yellow crystalline precipitate.

D. 75. Analysis of the Copper Group (P. 81–85).—The analysis of the copper group needs little discussion. The process adopted is that given in A. A. Noyes' Qualitative Analysis, except that cadmium and copper are separated by precipitating the former with hydrogen sulfide from cyanide solution, instead of by using the longer process (advantageous in elementary instruction) of precipitating the copper by metallic iron and the cadmium in the filtrate by hydrogen sulfide.

ANALYSIS OF THE TELLURIUM AND COPPER GROUPS

Tabular Outline VIII

See page 126.

Procedures and Notes

Procedure 70.—*Preparation of the Solution for the Hydrogen Sulfide Precipitation.*—Evaporate the filtrate from the HBr precipitate (P. 61) over a small flame until on removing the dish from the flame bubbles rapidly escape, but not until the $HClO_4$ fumes strongly. Cool the mixture, measure the volume of the remaining liquid, and add to it 25 cc. of water.

In case the solution is colorless, light-blue, light-green, or yellow, determine its acid-content by proceeding as follows. Add from a pipette or graduated dropper into each of three small crucibles just 1 cc. of methyl violet reagent (see Note 5). From a dropper add to one crucible 5 drops (0.17 cc.), and to another crucible 7 drops, of exactly 1 n. $HClO_4$ (see Note 6). Then to the third crucible add such a number of drops of the solution to be analyzed as will produce a color intermediate between that in the other two crucibles. (Take care, by using a suitable dropper and holding it always in the same position, that in all cases uniform drops are produced.) Calculate the acid-content of the whole solution, and the volume of 6 n. HCl (or 6 n. NH_4OH) that must be added to it to make its acid-content 30 milli-equivalents; and add to it this calculated volume of HCl (or NH_4OH).

In case the solution is red or dark-green, add enough 6 n. HCl (or 6 n. NH_4OH) to bring the acid-content to 30 milli-equivalents, considering that 9 milli-equivalents of $HClO_4$ are present in each cubic centimeter left after the evaporation.

Notes.—1. The solution from the HBr precipitation is evaporated to remove the HBr and $HCHO_2$. The escape of bubbles, which arise from decomposition of the remaining $HCHO_2$, furnishes a good indication of the nearly complete removal of these

acids, since this decomposition occurs only when the $HClO_4$ has become concentrated. The heating is stopped before the $HClO_4$ fumes strongly, so as to avoid reoxidation of iron, manganese, chromium, and vanadium to their higher valence states.

2. In order that the separation of the elements normally precipitated by H_2S from those not so precipitated may be sharp, it is essential that the acid concentration in the 100 cc. of solution in which the final precipitation is made (see P. 71) be in the neighborhood of 0.3 normal. It is most convenient to introduce the right quantity of acid at this point; and, when the solution does not have a color that interferes with the test, this quantity is conveniently determined with the aid of the indicator methyl violet, which in 25% C_2H_5OH undergoes a pronounced change of color from blue to green between 0.15 and 0.18 normal.

3. When, because of color in the solution, this indicator can not be employed, the acid-content has to be estimated, as well as may be, from the volume of the liquid left after the evaporation. This residual liquid may probably on an average be regarded as 9 n. $HClO_4$; but its composition doubtless varies much with the nature of the elements (coming from the original material) that are in solution in the acid.

4. The only elements that seriously interfere with this indicator test are those which, like cobalt, give a reddish color, and those which, like chromium, give an intense green color to the solution. Iron, copper, nickel, and uranium, even when 500 mg. are present in the $HClO_4$ solution, do not affect the color of the indicator so as to cause a change of more than one drop in the amount of 1 n. $HClO_4$ that has to be added in the indicator test (provided in the case of iron not more than half of it is in the ferric state, as is ordinarily the case). Small quantities of HBr and of $HCHO_2$, such as might remain after the evaporation, do not affect the color.

5. The methyl violet reagent is made up by dissolving 1 mg. of the indicator in 25 cc. of 95% C_2H_5OH and 75 cc. of water. Less alcohol causes the methyl violet to be precipitated by the $HClO_4$ contained in the solution to be tested. Much more alcohol makes it necessary to use a large amount of the tested solution.

6. The number of drops named in the Procedure are based on the use of an exactly 1 n. $HClO_4$ (which should be kept as a standard solution in the laboratory), on the use of a dropper delivering 30 drops per cubic centimeter, and on a particular methyl violet preparation. To meet possible variations in these conditions, the analyst should determine for himself the number of drops required to produce the most sensitive change in color;

which number should be such that a difference of two drops causes a marked change in color from bluish-green to green. Since the color of the indicator in the presence of acid fades noticeably within 3 minutes, the tests must be quickly made.

Procedure 71.—*Precipitation with Hydrogen Sulfide*—Add to the solution * prepared for the H_2S precipitation (P. 70) 4 cc. of 3 n. NH_4Cl, place it in a large test-tube set in boiling water, and pass through it a slow current of H_2S for 10 minutes. Cool the mixture, and saturate it with H_2S. Dilute it to 100 cc. with cold water, again saturate it with H_2S, and let it stand 15 minutes. (Precipitate, presence of TELLURIUM GROUP or COPPER GROUP.) Filter. Wash the precipitate with hot water.

In case iridium is to be tested for (see Note 7), or in case some molybdenum may still be unprecipitated (see Note 8), evaporate the filtrate to about 5 cc., and add to it (without filtering) just 10 cc. of 6 n. HCl. In case iridium is to be precipitated, boil the mixture with a return-cooler for 10 minutes. Cool the mixture, pour it into a 100-cc. pyrex bottle, add 5 cc. of water, and pass H_2S into it. While the bottle is filled with the gas, close it with a rubber stopper held securely in place by wiring it to the neck of the bottle, or by clamping the bottle in a pressure-bottle frame. Immerse the bottle in a vessel of water, and boil the water gently for half an hour. (If much dark precipitate separates, let the mixture cool, filter it, resaturate the filtrate with H_2S in the pressure-bottle, and heat it in boiling water for half an hour, or longer if the precipitate is increasing.) Let the mixture cool, and filter it. Wash the precipitates with hot water, and unite them with the previous one. Add to the filtrate just 10 cc. of 6 n. NH_4OH, and dilute it to 100 cc.

Treat the precipitate by P. 72.

Treat a part of the filtrate by P. 91, and the rest by P. 92.

* For practice-analyses use a solution made by mixing in a 50-cc. round pyrex flask test-solutions of tellurium, molybdenum, iridium, rhodium, and copper (1 cc. of each) with 5 cc. of 9 n. $HClO_4$, boiling the mixture (as in P. 5*B*) till 3 cc. remain, cooling, and adding 25 cc. of water. Treat the mixture (without filtering it) by P. 71–78.

Notes.—1. In order to secure by means of H_2S a good separation of the tellurium and copper groups from the elements of the following groups, careful attention must be given to the conditions of precipitation. The reasons for the operations prescribed in the first paragraph of the Procedure are given in Notes 2–6.

2. NH_4Cl is added before treating with H_2S, because zinc is less likely to be precipitated by H_2S from solutions containing chloride than from those in oxyacids alone, and because iridium, the most difficultly precipitated element of the tellurium group, is much more readily thrown down from chloride than from perchlorate solutions.

3. H_2S is passed into the solution when it is at nearly boiling temperature and when its volume is about 30 cc. and the free acid (HCl and $HClO_4$) is about 1 normal: (1) because the precipitation of molybdenum, iridium, and rhodium is promoted by high temperature and large concentration of the element; and (2) because zinc and indium, which are likely to be carried down with copper-group sulfides, are not so carried down so long as the acid is as strong as 1 n. For this last reason also the solution is cooled and again saturated with H_2S, so as to precipitate the copper group as completely as possible before the solution is diluted.

4. The solution is then diluted to 100 cc., thereby reducing the acid concentration to 0.3 normal, since at higher hydrogen-ion concentrations lead, bismuth, and cadmium are not completely precipitated. On the other hand a much lower acid concentration can not be employed, since it would lead to the precipitation of zinc, indium, nickel, and cobalt, when much of them is present, even in the absence of copper-group elements.

5. Under the conditions discussed in the preceding Notes all the elements of the tellurium and copper groups are completely precipitated with the exceptions that most of the iridium may remain in solution, and that, when the solution contains a large quantity of molybdenum (owing to the simultaneous presence of phosphate), a considerable part (10–30% of 300 mg.) may remain dissolved, in which case it gives a deep-blue color to the solution.

6. Moreover, under these conditions, none of the elements of any of the following groups passes into the H_2S precipitate in considerable proportion (in relation to the total quantity of the element present). Thus even 500 mg. of zinc, iron, nickel, or cobalt, and 100 mg. of indium or gallium do not precipitate when present alone; and even 1 or 2 mg. of any of them, when present with large quantities of copper-group elements, can be detected in the filtrate. Also under these conditions titanium remains in solu-

tion; though it would precipitate slowly as H_2TiO_3 at 90–100° if the solution so heated were only 0.3 n. in acid.

7. Iridium and rhodium are very rarely found except in ores or alloys from special sources, and then they are almost always associated with some of the other platinum elements. It is therefore usually desirable to test for iridium and rhodium only when the source of the material makes their presence seem possible, and even then, only when some of the other platinum elements, osmium, ruthenium, platinum, and palladium, have been detected in the earlier stages of the analysis. Hence provision has to be made for ensuring more complete precipitation of iridium only in rare cases.

8. The case in which molybdenum is present with phosphate, and in which therefore molybdenum may be found in the filtrate from the H_2S treatments in an open vessel, is also a rare one. Moreover, it is indicated by the formation of a yellow precipitate of ammonium phosphomolybdate on the addition of NH_4Cl at the beginning of this Procedure, and by a blue coloration of the filtrate from the first H_2S treatments. It is therefore necessary to treat the filtrate by the supplementary process described in the second paragraph of the Procedure for the sake of ensuring complete precipitation of molybdenum only when these indications are obtained.

9. The supplementary process just mentioned is much more effective for precipitating iridium than the previous treatments, because after the heating with strong $HClO_4$ the iridium is in the form of perchlorate, and from this it is much more slowly precipitated by H_2S than from the chloride, into which it is gradually converted by the boiling with strong HCl; and because the solution is more concentrated both in H_2S and in the iridium in the treatment in the pressure-bottle than it is in the open vessel. Under the prescribed conditions about 90% of the iridium may be precipitated by one hour's heating under pressure.

10. The precipitation of the molybdenum is much more rapid in the pressure-bottle treatment mainly because of the higher concentration of the H_2S and of the molybdenum. When treated in the way described, some of the molybdenum precipitates during the evaporation of the solution, and the remainder usually comes down completely after a half-hour's heating in the pressure-bottle. This is true even when large quantities of molybdenum and phosphate are simultaneously present.

11. When the pressure treatment is used a measured volume of

HCl (10 cc. of 6 n.) is added; and at the end this is neutralized by adding an equal volume of 6 n. NH_4OH, in order that the concentration of free acid may be suitable for the subsequent treatment in P. 92. For the same reason the solution is finally diluted to 100 cc.

TELLURIUM GROUP

Procedure 72.—*Dissolving of the Sulfides and Precipitation of Tellurium.*—Heat the H_2S precipitate (P. 71) in a casserole with 5–10 cc. of 12 n. HCl on a steam-bath for 5 minutes; add 1–2 cc. of 16 n. HNO_3, and heat the mixture to 60–70° till the residue dissolves or becomes light-colored. Evaporate the mixture just to dryness. Treat the residue with just 6 cc. of 12 n. HCl, and saturate the (cold) mixture with SO_2 gas. Filter out and reject any residue. Transfer the solution to a large test-tube, add to it just 20 cc. of water, saturate it with SO_2 gas, and heat it in boiling water for 15 minutes. (Black precipitate, presence of TELLURIUM.) Filter the hot mixture.

Treat the filtrate by P. 73.

Treat the precipitate no further.

Notes.—1. The H_2S precipitate is first heated with 12 n. HCl to dissolve the copper-group sulfides, all of which (except CuS) are readily acted upon by this solvent; thereby avoiding so far as possible liberation of sulfur in the subsequent treatment with HNO_3. Heating with the mixed acids is necessary, however, in order to dissolve the tellurium-group precipitate. In case of the sulfides of iridium and rhodium a fairly long treatment may be required. Heating on a steam-bath is preferable to boiling, as always in aqua-regia treatments, since boiling causes the two acids to destroy each other and the chlorine thereby produced to be expelled, before it has time to act upon the precipitate.

2. The solution is evaporated to destroy all the HNO_3, which otherwise would oxidize some of the H_2SO_3 later added. The residue is treated with 12 n. HCl and the cold solution saturated with SO_2, in order to remove any selenium which might be present owing to its incomplete volatilization in the HBr distillation. Tellurium is not precipitated by H_2SO_3 from a cold solution in 12 n. HCl.

3. The solution is diluted so that the HCl becomes about 2.7 n.,

since at this concentration the tellurium is most rapidly precipitated by H_2SO_3. Under these conditions, after heating in boiling water for 15 minutes, 0.5 mg. of it gives a precipitate, and 100 mg. are completely precipitated. It separates as a black powder. With a small quantity the solution is only darkened at first, but a precipitate settles out on standing.

4. None of the other elements that can be present is reduced to the metallic state or precipitated as chloride under these conditions. Any quantity of lead that can be present (thus even 50 mg.) remains in solution, since $PbCl_2$ and $PbSO_4$ are fairly soluble in hot 3 n. HCl.

Procedure 73.—*Extraction of Molybdenum with Ether.*—Evaporate the H_2SO_3 solution (P. 72) almost to dryness. Add to the residue a few drops of 16 n. HNO_3, and evaporate the mixture to dryness on a steam-bath. Add 5 cc. of 6 n. HCl, and (without filtering out any residue) shake the solution for 2 or 3 minutes successively with two 15-cc. portions of ether in a short-stem separating funnel (see Note 4, P. 51). Unite the ethereal extracts, wash them by shaking successively with two 2-cc. portions of 6 n. HCl, and reject the washings.

Treat the ethereal solution by P. 74.

Treat the aqueous solution by P. 75, in case iridium and rhodium are to be tested for. Treat it by P. 81, in case iridium and rhodium are not to be tested for.

Notes.—1. The filtrate from the H_2SO_3 treatment is evaporated almost to dryness so as to enable the residue to be taken up in HCl of definite concentration. The residue is first heated with HNO_3 to reoxidize any molybdenum that may have been reduced by the H_2SO_3. Lead will not be present in considerable quantity; but if any $PbCl_2$ remains undissolved on adding the 5 cc. of 6 n. HCl, it need not be filtered off, since it does not interfere with the ether extraction.

2. In the extraction a small volume of the HCl is shaken with a larger volume of ether, since the distribution-ratio is not very favorable. Thus, under the specified conditions only about 85% of the molybdenum passes into the ether on the first shaking; but even so, only about 2–3% of it remains in the aqueous layer after the second shaking. This does not appreciably affect the estimate of the quantity of molybdenum present, nor does it interfere with

the subsequent analysis of the aqueous solution. The substance extracted by the ether is $MoO_3 ; 2HCl$. As the extraction of the various elements doubtless depends on the HCl concentration, the directions of the Procedure should be followed; thus 6 n. HCl and ether not previously shaken with it should be used.

3. The ether solution is washed with a little 6 n. HCl to remove from it small quantities of elements other than molybdenum. Thus copper and rhodium dissolve sufficiently to color the ether layer, and cadmium dissolves appreciably; but all these elements are removed by the washing with 6 n. HCl.

4. Not more than 2–3 mg. of molybdenum will ordinarily be found at this point, even when a large quantity was originally present; for nearly all of it remains with the tungsten and tantalum groups after the evaporation with $HClO_4$. Only when phosphate is also present will the molybdenum, owing to the formation of phosphomolybdic acid, pass largely or entirely into the $HClO_4$ solution and therefore into the H_2S precipitate.

Procedure 74.—*Detection of Molybdenum.*—Evaporate the ethereal solution (P. 73) to dryness in a casserole on a steam-bath, and dry the residue completely by warning it over a small moving flame. (Dark-blue residue, presence of MOLYBDENUM.)

In case the residue is blue, add to it 2 cc. of 12 n. HCl and 0.5 cc. of 6 n. HNO_3, and evaporate again to dryness on a steam-bath. Dissolve the residue in 2 cc. of 6 n. HCl, and add 5 cc. of water and 5 cc. of 1 n. KSCN. (If there is a deep-red color, make the solution alkaline with 6 n. NaOH, heat it nearly to boiling, filter out the precipitate, neutralize the solution with 6 n. HCl, and add 2 cc. more.) Add about 0.1 cc. of finely granulated Zn. (Red color, increasing for some minutes, presence of MOLYBDENUM.) If an increasing red color results, decant the solution from the Zn into a test-tube, place the tube in boiling water, and pass a slow current of H_2S through it for 10 minutes. (Brown precipitate, presence of MOLYBDENUM.)

Notes.—1. The dark-blue color of the residue is an extremely delicate indication of molybdenum, even 0.1 mg. of it giving a distinct color; and when no color results, further testing for

molybdenum is unnecessary. In order that the conclusion may be reliable, however, the residue obtained on evaporating the ethereal solution must be dried completely by heating it gently over a small flame. The blue substance is probably "molybdenum blue," a molybdate of quinquivalent molybdenum (see Note 2, P. 36). It is produced by reduction of $MoO_3 \cdot 2HCl$, probably by organic substances coming from the ether.

2. As to the KSCN test for molybdenum and the need of guarding against the presence of iron, see Notes 1 and 2, P. 38.

3. The final precipitation with H_2S affords a further assurance that the red color produced by KSCN is not due to iron. It serves mainly, however, to make possible an estimate of the quantity present, which it is difficult to do by either of the color tests.

Procedure 75.—*Separation of the Copper Group from Iridium and Rhodium.*—Evaporate the aqueous solution from the ether extraction (P. 73) just to dryness. Add 1 cc. of 6 n. $HC_2H_3O_2$, 10 cc. of water, and 5 cc. of 3 n. $NaNO_2$; and heat the mixture for 5 minutes at 60–70°. Cool; and, without filtering out any precipitate, add 6 n. NaOH, 0.5 cc. at a time, with vigorous stirring, till the solution turns litmus paper deep-blue, diluting with 10–20 cc. of water during the neutralization if a large precipitate separates. (Precipitate, presence of COPPER GROUP.) Filter the mixture. Wash the precipitate with hot water. To the filtrate add 5 cc. of 1 f. $NaHCO_3$; and, if there is a precipitate, filter it off on a separate filter, wash it, and unite it with the previous one.

Dissolve the precipitate in 3–6 cc. of 6 n. HNO_3, and analyze the solution for the copper group by P. 81–85.

Treat the filtrate by P. 76.

Notes.—1. This separation depends on the facts that all the elements of the copper group (lead, bismuth, cadmium, and copper) are precipitated by NaOH in small excess; and that iridium and rhodium are not so precipitated, provided they have been converted by heating with $NaNO_2$ into their complex nitrites, $Na_3Ir(NO_2)_6$ (sodium iridonitrite) and $Na_3Rh(NO_2)_6$ (sodium rhodonitrite).

2. A slight acidity promotes the reduction of iridium from the quadrivalent to the trivalent state and the complete conversion of it and of rhodium into the complex nitrite. The solution from

the ether extraction is therefore evaporated to dryness, and 1 cc. of 6 n. $HC_2H_3O_2$ (rather than of a strong acid) is added, so as to produce only a small concentration of H^+ and therefore of free HNO_2. Warming also promotes the formation of the complexes. Too great acidity or too much heating is unfavorable, since the free HNO_2 is thereby rapidly decomposed. The complete conversion of these elements into their nitrites is shown by the production of a pure yellow solution; but this color may not be visible unless as much as 15–20 mg. is present.

3. In order to secure complete precipitation of lead, much excess of NaOH is avoided; and after filtering $NaHCO_3$ is added, since under these nearly neutral conditions scarcely any of the slightly soluble $PbCO_3$ is converted into soluble $NaHPbO_2$. The $NaHCO_3$ is not added till after the mixture has been filtered, since otherwise much copper dissolves, forming a deep-blue solution, owing to production of a soluble complex salt, such as $NaHCu(CO_3)_2$, with the $NaHCO_3$ in the solution. Some $Bi(OH)_3$ may precipitate, owing to hydrolysis of its salts in the $HC_2H_3O_2$ solution, before the NaOH is added.

4. The separation is fairly satisfactory with respect to iridium and rhodium. Thus, when treated by the Procedure, 100 mg. of iridium or rhodium, when present alone, remain in solution (except that 1–2 mg. of rhodium may separate as a turbidity). And, when 1–2 mg. of iridium or rhodium are present even with a large quantity of copper-group elements (thus with 500 mg. of copper or with a mixture of 200 mg. each of bismuth, cadmium, and copper), more than half of the iridium and all of the rhodium pass into the filtrate. On the other hand, even though nitrite is present, 50 mg. of lead, and 500 mg. of other copper-group elements are completely precipitated; and even 1 mg. of any of them gives a precipitate.

Procedure 76.—*Precipitation of Iridium and Rhodium.*—Add to the filtrate from the nitrite treatment (P. 75) 5 cc. of 12 n. HCl, and evaporate the solution just to dryness, taking care not to overheat the residue. Dissolve the residue in 15 cc. of water, and add to it 2 cc. of 3 n. Na_2CO_3. Heat the solution in a test-tube for 5 minutes in a boiling water-bath. Cool the mixture, add to it (without filtering) 2 cc. of 3 n. Na_2CO_3 and 2 drops of liquid Br_2, and shake till the Br_2 dissolves. If there is much precipitate, add 2–4 drops more of Br_2. Heat

the mixture in boiling water for 10 minutes, cool it, and add a drop of liquid Br_2. (Blue-black precipitate, presence of IRIDIUM; green precipitate, presence of RHODIUM.) Filter, and wash the precipitate thoroughly with hot water. If the filtrate is blue or green, heat it in a test-tube in boiling water for half an hour, cooling it from time to time and adding a drop of liquid Br_2. Filter out any precipitate, wash it, and unite it with the previous one.

Treat the precipitate by P. 77. Reject the filtrate.

Notes.—1. This Procedure serves to show at once whether iridium or rhodium is present, and to separate these elements, when present, from the large quantity of salt in the solution. The complex nitrites are first decomposed by boiling with HCl; the H_3IrCl_6 and H_3RhCl_6 resulting are then converted, by heating with Na_2CO_3, into soluble $NaIrO_2$ (sodium iridite) and into precipitated light-yellow $Rh(OH)_3$; and finally the trivalent iridium and rhodium are oxidized, by the Br_2 added and the NaBrO thereby formed, to the insoluble hydrated dioxides, IrO_2 and RhO_2, which are bluish-black and green respectively. Under the conditions of the Procedure 1 mg. of iridium or rhodium gives a precipitate.

2. To ensure decomposition of the complex nitrites, the solution is made strongly acid with HCl and boiled till it is all evaporated. This also removes the excess of acid, which otherwise would have to be neutralized; thereby avoiding the production of a large amount of salt which retards the precipitation of iridium and rhodium.

3. After addition of the Na_2CO_3 the solution is heated; for otherwise, probably owing to incomplete decomposition of the chloroiridite and chlororhodite, rhodium is not precipitated as yellow $Rh(OH)_3$, and iridium may not be precipitated on the later addition of Br_2 when only a little is present. A large excess of Br_2 decreases the delicacy of the rhodium precipitation; hence, unless much rhodium or iridium is present, only two drops of liquid Br_2 are added. The subsequent heating serves to coagulate the precipitate. Prolonged heating may, however, cause the precipitate to redissolve, owing to decomposition of the NaBrO.

4. When much iridium or rhodium is present, a part of it remains unprecipitated and imparts a blue (or green) color to the

solution. Continued heating with occasional addition of Br_2 may cause its coagulation, especially when only a small quantity is present. If after a half-hour's heating the liquid is still deeply colored, complete precipitation can best be secured by evaporating the mixture with HCl, to reconvert the iridium and rhodium into chlorides, and repeating the other operations of the Procedure. This is unnecessary, however, since by far the larger proportion of these elements is always precipitated, and since the filtrate is treated no further.

Procedure 77.—*Separation of Iridium from Rhodium.*—Heat the NaBrO precipitate (P. 76) in a small casserole with 1–3 cc. of 9 n. HBr on a steam-bath till it dissolves. Add 3 cc. of 12 n. HCl and 1 cc. of 16 n. HNO_3, and evaporate the solution just to dryness. To the residue add 1 cc. of 12 n. HCl, and evaporate again just to dryness. Add 2 drops of 6 n. HCl, and transfer the mixture to a weighing bottle with not more than 1–2 cc. of water. Saturate the solution with Cl_2, stopper the bottle, and heat it at about 50° for five minutes. Cool, add powdered NH_4Cl with constant agitation till no more of it dissolves, avoiding much excess. Heat the mixture on a steam-bath for 15 minutes. Cool it, saturate it with Cl_2, and let it stand 15 minutes. If no precipitate is visible, give the bottle a gentle rotary motion to cause any particles to gather in the center. (Dense black precipitate, presence of IRIDIUM; red solution, presence of RHODIUM.) If there is much precipitate, decant the liquid, heat it on a steam-bath for 15 minutes, cool it, saturate it with Cl_2, and let it stand 15 minutes, repeating these operations till no more precipitate separates. Filter the mixture through a very small filter; and wash the filter with 1 cc. of cold 3 n. NH_4Cl, adding the washings to the filtrate.

Treat the precipitate no further.

Treat the filtrate, if colored, by P. 78.

Notes.—1. The NaBrO precipitate (of IrO_2 and RhO_2) is heated with 9 n. HBr, since this acid, owing to its powerful reducing action, dissolves it more readily than HCl or HNO_3. The solution is evaporated with HCl and HNO_3 to destroy the

bromide, and to oxidize the iridium to the quadrivalent state. It is then evaporated with HCl alone to ensure complete removal of the HNO_3.

2. The detailed operations of the Procedure serve to secure the precipitation of a small quantity of $(NH_4)_2IrCl_6$, which is somewhat soluble in water and tends to form supersaturated solutions. The residue after evaporation is dissolved in not more than 2 cc. of slightly acidified water. The solution is saturated with Cl_2 and warmed to 50°, in order to ensure oxidation of the iridium to the quadrivalent state; a higher temperature being avoided, since the Cl_2 is then more rapidly destroyed by action on the NH_4Cl (with formation of N_2 and HCl). The solution is cooled and saturated with NH_4Cl to diminish the solubility of the complex salt (through the common-ion effect). The solution is finally warmed, since this has been found to promote the separation of the precipitate.

3. Under the conditions of the Procedure, when the final volume of the mixture is 2 cc., 0.2–0.4 mg. of iridium yields a precipitate. When a large quantity (50 mg. or more) is present, precipitation takes place slowly, and several hours are required to secure a fairly complete precipitation; even then some of it may remain in solution, but not enough to precipitate in the subsequent rhodium test. Even 100 mg. of rhodium remain in solution. Even 1 mg. of rhodium gives a pink color to 2 cc. of water saturated with NH_4Cl; so that a colorless filtrate need not be further tested.

Procedure 78.—*Confirmation of Rhodium.*—To the filtrate from the NH_4Cl precipitate (P. 77) in a small casserole add 3 cc. of 15 n. NH_4OH, and evaporate the solution to dryness on a steam-bath. To the residue add 2–3 cc. of 6 n. HCl, bring the mixture to boiling, transfer it to a weighing bottle, and let it stand at least half an hour. If any NH_4Cl separates, add just enough cold water to dissolve it. (Light-yellow residue, presence of RHODIUM.)

Notes.—1. $(NH_4)_3RhCl_6$ (ammonium chlororhodite) is converted by heating with hot strong NH_4OH into $RhCl(NH_3)_5^{++}Cl^-_2$ (chloro-pentammino-rhodium chloride), which remains undissolved on adding cold 6 n. HCl. It is heated with this acid, which, when hot, dissolves it in moderate quantity, since it then separates on cooling as a fine yellowish-white crystalline powder. A precipi-

tate results even when only 0.5 mg. of rhodium is present in 2 cc. of solution. When a large quantity is present, a large bright-yellow precipitate forms, and the solution above it is deep-yellow, even though the precipitation be nearly complete. Iridium, at any rate in quantity up to 5 mg., remains in solution.

2. If only a small white precipitate separates, this may consist of silica introduced from the vessels or reagents. This is distinguished from a small quantity of the rhodium compound by its not dissolving on heating with HCl.

COPPER GROUP

Procedure 81.—*Separation of Lead from Bismuth, Copper, and Cadmium.*—To the HNO_3 solution of the copper group (P. 75), or to the HCl solution of it from the ether extraction (P. 73), add 3 cc. of 18 n. H_2SO_4; and evaporate it in a casserole till dense white fumes of H_2SO_4 begin to come off, adding 2 cc. more 18 n. H_2SO_4 if a large residue separates during the evaporation. Cool the mixture; pour it, a little at a time, into 10 cc. of cold water in a test-tube, cooling the tube after each addition; rinse out the casserole with the same solution; cool the mixture, and let it stand 5 minutes, but not much longer. (Fine white precipitate, presence of LEAD.) Filter, and wash the precipitate first with 2 n. H_2SO_4, and then with about 5 cc. of water.

Treat the precipitate by the second paragraph of P. 63, to confirm the presence of lead.

Treat the filtrate by P. 82.

Notes.—1. The solution is evaporated with H_2SO_4 in order to expel the HNO_3 or HCl, which if not removed would dissolve some $PbSO_4$ and diminish the delicacy of the test for lead. A fairly large quantity of H_2SO_4 is added, so as to diminish the solubility of $PbSO_4$, and so as to hold bismuth in solution when a large quantity of it is present.

2. The mixture is allowed to stand a few minutes so as to ensure complete precipitation of the lead; for the solutions of $PbSO_4$ tend to remain supersaturated. It is not allowed to stand longer; for otherwise, when much bismuth is present, it may separate as a coarsely crystalline precipitate of $(BiO)_2SO_4$, to such extent that not more than 50 mg. of bismuth remain in solu-

tion. It is with the purpose of holding a large quantity of bismuth in solution that special care is also taken to keep the mixture cool during the dilution of the H_2SO_4; for heating tends to break up the state of supersaturation.

3. If in spite of these precautions a coarsely crystalline precipitate separates, it should, before applying the confirmatory test for lead, be dissolved in 5–10 cc. of 6 n. HCl, and the solution treated again by P. 81. The smaller quantity of bismuth now present in the solution is not likely to precipitate on diluting the H_2SO_4 solution with water. Any $PbSO_4$ present is dissolved by the HCl; and this acid must be all evaporated off to ensure complete reprecipitation of the lead.

4. The confirmatory test for lead with K_2CrO_4 should not be omitted, since the H_2SO_4 precipitate might consist of alkaline-earth sulfate (see Note 1, P. 63) or of $(BiO)_2SO_4$. Any small quantity of the latter dissolves in $NH_4C_2H_3O_2$ solution, but gives no precipitate with K_2CrO_4 in the presence of $HC_2H_3O_2$.

Procedure 82.—*Separation of Bismuth from Copper and Cadmium.*—To the filtrate from the H_2SO_4 precipitate (P. 81) add 6 n. NH_4OH, 1 cc. at a time, till the mixture after shaking smells of it. (White precipitate, presence of BISMUTH; blue solution, presence of COPPER.) Filter the mixture, and wash the precipitate thoroughly with hot water.

Treat the precipitate by P. 83. Treat the filtrate by P. 84.

Notes.—1. The precipitate produced by NH_4OH may consist of $Fe(OH)_3$ or of other hydroxides of later groups, if these elements were not removed from the H_2S precipitate by thorough washing. The formation of a small precipitate is therefore not a sufficient proof of the presence of bismuth; and the confirmatory test of P. 83 should always be applied.

Procedure 83.—*Confirmation of Bismuth.*—Pour through the filter containing the NH_4OH precipitate (P. 82) a cold freshly prepared solution of Na_2SnO_2 (sodium stannite) (see Note 1). (Immediate blackening of the residue, presence of BISMUTH.)

Notes.—1. The solution of sodium stannite (Na_2SnO_2) is prepared when needed by adding 6 n. NaOH, a few drops at a time, to 8–10 drops of 1 n. $SnCl_2$ diluted with 3 cc. of water (the

mixture being cooled in running water after each addition), till the large precipitate of $Sn(OH)_2$ first formed is dissolved and a clear or slightly turbid liquid results. The solution must be kept cold while it is being prepared, and it must be freshly prepared, because the stannite decomposes spontaneously into stannate (Na_2SnO_3) and metallic Sn, and because it oxidizes in contact with air to stannate.

2. The test with Na_2SnO_2 depends on the reduction of $Bi(OH)_3$ to black metallic Bi. The test is an extremely delicate one. The other reducible substances, like $HSbO_3$, $Fe(OH)_3$, $Pb(OH)_2$, or $Cu(OH)_2$, that might possibly be present in the NH_4OH precipitate are not reduced by short contact with Na_2SnO_2 solution in the cold. Mercury, if present, would cause blackening; but it is not precipitated by NH_4OH in the presence of ammonium salt.

Procedure 84.—*Confirmation of Copper.*—Acidify one fourth of the NH_4OH solution (P. 82) with 6 n. $HC_2H_3O_2$, add from a dropper one drop of 1 n. $K_4Fe(CN)_6$, and let the mixture stand 2–3 minutes. (Red precipitate, presence of COPPER.) Then add 3 cc. more 1 n. $K_4Fe(CN)_6$.

Notes.—1. The confirmatory test for copper is more delicate than the formation of a blue color with NH_4OH in P. 82. It should, therefore, be tried even when the NH_4OH solution is colorless. Cadmium is also precipitated by $K_4Fe(CN)_6$; but the precipitate is white, and does not prevent the pink color of the copper compound from being detected, provided only a small quantity of $K_4Fe(CN)_6$ is added, and the mixture is allowed to stand; for the copper salt, owing to its smaller solubility, is precipitated immediately or formed rapidly by metathesis from the precipitated $Cd_2Fe(CN)_6$. The larger quantity of the reagent subsequently added affords an estimate of the quantity of copper except when much cadmium is present.

2. Aside from copper, only uranium and molybdenum give red precipitates with $K_4Fe(CN)_6$ in acid solution; but they do not do so from a solution only weakly acid with acetic acid, as in the Procedure. Nickel, which gives a blue solution with NH_4OH, gives a light-green precipitate with $K_4Fe(CN)_6$.

Procedure 85.—*Detection of Cadmium.*—To the remainder of the NH_4OH solution (P. 82) add enough 1 n. KCN to decolorize it (if it is blue); then 5–10 drops more. (See Note 1.)

Pass into the mixture a moderate current of H_2S gas for about half a minute. (Immediate yellow precipitate, presence of CADMIUM.)

Notes.—1. In working with KCN bear in mind that it is extremely poisonous. Take care not to acidify solutions containing it, except with great precautions, since gaseous HCN then escapes.

2. The presence of cadmium is shown by the immediate formation of a yellow precipitate by the H_2S, but not by a yellow coloration of the solution nor by the separation of a precipitate upon standing. For, when much copper is present and the solution is saturated with H_2S and allowed to stand, the solution soon becomes of a deep-yellow color and an orange-red crystalline precipitate may later separate from it, owing to the fact that the orange-red compound $(CSNH_2)_2$ is formed by union of the H_2S with the $(CN)_2$ set free by the decomposition of the $Cu(CN)_2$.

3. In case a small black precipitate is produced in this test, and this prevents a positive conclusion as to the presence or absence of a little cadmium, the precipitate may be treated, in order to eliminate the black sulfide, as follows. Filter out the precipitate, wash it thoroughly, rinse it into a casserole with about 15 cc. of 1.2 n. H_2SO_4, cover the casserole, boil the mixture gently for 5 minutes, filter it, cool the filtrate, add to it three times its volume of water, and pass H_2S into it for 5–10 minutes. A yellow precipitate of CdS will then be obtained if cadmium is present.

Tabular Outline IX

PRECIPITATION OF THE ALUMINUM, NICKEL, ZIRCONIUM, AND RARE-EARTH GROUPS. ISOLATION OF THE ALUMINUM GROUP. DETECTION OF IRON, PHOSPHATE, AND GALLIUM.

FILTRATE FROM THE HYDROGEN SULFIDE PRECIPITATE (P. 72).

Test a small portion for iron and phosphate (P. 91).

Boil the remainder (to expel H_2S), *add* Br_2, *then* $NH_4C_2H_3O_2$ *and* $Fe(NO_3)_3$, *and heat (P. 92).*

Precipitate: Fe, Ga, Cr, V, W, Al, In, Zr, Ti, PO_4, †Zn, †Co, †Ni, †Be, †U; basic elements as hydroxides, basic acetates, phosphates or vanadates; also ‡RE (in case PO_4 is present).

Dissolve in HCl, evaporate, add 7 n. HCl, shake with ether (P. 93).

Filtrate: Mn, Zn, Co, Ni, U, Be, RE[a], AE[a], Ak[a], †Cr.

Add NH_4OH *and* H_2S *(P. 96).*

Ether layer: $FeCl_3$, $GaCl_3$.

Evaporate, add HCl, shake with Hg (P. 94).

Filtrate: $FeCl_2$, $GaCl_3$.

Shake with ether (P. 94).

Water layer: $FeCl_2$. *Reject.*

Ether layer: $GaCl_3$, †$FeCl_3$. *Remove Fe with NaOH, acidify, test for gallium (P. 94).*

Precipitate: Hg_2Cl_2, Hg. *Reject.*

Water layer: Cr, V, W, Al, In, Zr, Ti, PO_4, Zn, Co, Ni, Be, U, RE.

Evaporate with HNO_3, *boil with* $NaOH$ *and* Na_2O_2 *(P. 95).*

Precipitate: Be, RE, Cr, as hydroxides; Mn, Zn, Co, Ni, U, as sulfides.

Dissolve in HNO_3, *evaporate, boil with* $NaOH$ *and* Na_2O_2 *(P. 97).*

Filtrate: AE, Ak. See T. XIII.

Precipitate: ZIRCONIUM GROUP: In, Zr, Ti, as hydroxides. Also RE, Co, Ni, †Zn. See T. XI.

Filtrate: ALUMINUM GROUP: Cr, U, V, W, Al, Be, Zn, as sodium salts. Also PO_4. See T. X.

Filtrate:

Precipitate: NICKEL GROUP: Mn, Co, Ni. RARE-EARTH GROUP: Sc, Th, Ce, La, Pr, Nd, Sm, Y, Eu-Lu. Also ‡Zn. See T. XI.

[a] By the symbol RE are denoted the elements of the rare-earth group; and by AE and Ak the alkaline-earth and alkali elements.

* † ‡ For the significance of these signs see page 9.

PRECIPITATION AND PARTIAL ISOLATION OF THE ALUMINUM, NICKEL, ZIRCONIUM, AND RARE-EARTH GROUPS

With Ernest H. Swift

Tabular Outline IX

See page 148.

General Discussion

D. 91. Elements Involved and their Grouping in this System of Analysis.—The elements still present in the solution, aside from those of the alkaline-earth and alkali groups, classified in accordance with the scheme of analysis adopted, are as follows:

Detected separately: Fe, Ga, PO_4.
Aluminum group: Cr, U, V, ‡W, Al, Zn, Be.
Nickel group: Mn, Co, Ni.
Zirconium group: In, Zr, Hf, Ti.
Rare-earth group: { Sc, Th, Ce. / Lanthanum subgroup, La, Pr, Nd, Sm, Eu. / Yttrium subgroup, Y, Gd, Tb, Dy, Ho, Er, Tu, Yb, Lu.

D. 92. Precipitation of the Elements by Successive Treatments with Ammonium Acetate and Sulfide (*P. 92, 96*).—The addition of ammonium hydroxide and sulfide to the solution would cause complete precipitation of nearly all the elements. This is not true, however, of gallium, vanadium, and tungsten, except when present with other elements, such as iron, which carry them down. Thus, when present alone, considerable gallium dissolves in excess of ammonium hydroxide, vanadium is precipitated only partly, if at all, either by ammonium hydroxide or sulfide, and tungsten is not precipitated at all by these reagents. Moreover, when phosphate is present, these reagents precipitate also the alkaline-earth elements, which cause complications in the later analysis, especially in the isolation of the rare-earth group as fluorides.

‡ Tungsten is found at this point only when it is accompanied by phosphate.

The most convenient way of separating the alkaline-earth elements from phosphate is to use the familiar method of adding a ferric salt to a hot weakly acid ammonium acetate solution. A study was therefore made of the behavior of gallium, vanadium, and tungsten under the conditions of this process. As it was found that a complete precipitation of these elements could be realized by this method, it was adopted as a part of the general procedure. This was all the more justified by the facts that iron and phosphate can be tested for in a small portion of the filtrate from the hydrogen sulfide precipitate, and that the iron added as reagent in the acetate process can later be readily removed by extraction with ether from a hydrochloric acid solution, so that it does not affect the subsequent separations.

Having attained by the acetate process with the aid of ferric iron the separation of phosphate from alkaline earths and the precipitation of gallium, vanadium, and tungsten, it is natural to employ ammonium hydroxide and sulfide to complete the precipitation of chromium and aluminum, and to bring down the rare earths and the bivalent elements of the aluminum and nickel groups. Under the procedure adopted less than 0.5 mg. of any of these elements remains in the filtrate from the sulfide precipitate.

It will be seen from the tabular outline that the acetate and sulfide precipitates do not consist of two sharply differentiated groups of elements, inasmuch as several of the elements may be found partly in one precipitate and partly in the other, and must therefore be tested for in both places. The two precipitations, however, serve (1) when taken together, to assure the complete precipitation of all the elements involved, and (2) to separate fairly completely some of the elements from each other (for example, iron and elements of the zirconium-group from those of the nickel group), whereby the process of analysis is made simpler.

D. 93. The Acetate Precipitation (P. 92).—The acetate process was used in the following form. To the filtrate from the hydrogen sulfide precipitate (after expelling the sulfide and oxidizing with bromine any ferrous salt present) enough ammonium hydroxide and acetate was added to produce such a hydrogen-ion concentration as would cause iron and gallium to be precipitated completely and alkaline-earth phosphates to be retained in solu-

tion; then enough ferric nitrate was introduced to combine with any phosphate and to carry down any vanadium and tungsten present; and the mixture was boiled and filtered. When a large quantity of precipitable elements, especially of aluminum, is present, the precipitation of the iron may be incomplete, owing to the acid produced by the metathesis; in that case enough more ammonium hydroxide is added to restore the acidity to approximately its original value. Under these conditions the trivalent and quadrivalent elements, aluminum, chromium, indium, zirconium, and titanium, are also precipitated completely or nearly so, while the bivalent elements (including uranium in the uranyl state) are in general carried down to only a small extent. The rare-earth elements, which are not precipitated when present alone, were found to have the remarkable effect of preventing the precipitation of the iron. This difficulty was, however, overcome by adding an amount of phosphate nearly equivalent to the rare earths present; whereby these are completely or largely precipitated, enabling the iron also to separate.

D. 94. Removal of Iron and Detection of Gallium (P. 93, 94). —From the other elements in the acetate precipitate the iron and gallium are first removed by shaking the solution of that precipitate in 6.5 n. hydrochloric acid with ether. That iron can be so extracted is well known: indeed, upon this fact a quantitative process of separation is based. This initial removal of the iron (both that added as a reagent and any originally present in the material analyzed) has the advantage that the precipitate later produced by sodium hydroxide and peroxide is smaller in size, and carries down to a less extent elements of the aluminum group.

The discovery, made by Dr. E. H. Swift, that gallium is shaken out of aqueous hydrochloric acid by ether afforded a welcome solution of the difficult problem of separating and detecting this element. It was found that its separation from nearly all the iron could be readily accomplished by evaporating the ethereal solution, dissolving the residue in hydrochloric acid, reducing the iron to the ferrous state by shaking the solution with mercury, and again extracting the gallium with ether. After removing with sodium hydroxide any small amount of iron still remaining, the gallium is detected by an acetate precipitation, and its presence in the precipitate is confirmed by testing with potassium ferrocyanide.

D. 95. Separation of the Aluminum Group from the Other Elements in the Acetate Precipitate and in the Sulfide Precipitate (P. 95, 97).—This title shows the object of the next operation in the analysis both of the acetate precipitate and of the sulfide precipitate. This object is attained by treating with sodium hydroxide and peroxide the solutions of the two precipitates separately. Thereby all the elements of the aluminum group are converted into soluble sodium salts. The peroxide is added in order to dissolve chromium and uranium by converting them into chromate and peroxyuranate. All the elements of the other groups are completely precipitated by these reagents, though this is true of titanium, owing to its initial conversion to some extent into peroxytitanate, only after the mixture has been boiled for some minutes. The solutions of the acetate and sulfide precipitates are not united, but are treated separately with the reagents so as not to sacrifice the advantages of the partial separation already affected by the acetate precipitation. The main advantage is that the zirconium group has been largely separated from the nickel group, the former usually passing almost wholly into the acetate precipitate, and the latter into the sulfide precipitate. An incidental advantage is that titanium has been largely separated from uranium, making it possible, by longer boiling of the part containing the titanium, to ensure its complete precipitation by destruction of the peroxytitanate, and by shorter boiling of the part containing the uranium, to retain it all in solution as peroxyuranate.

MODIFICATIONS OF THE PROCESS INVESTIGATED

D. 96. Inadequacy of Ammonium Hydroxide Separations.— In some schemes of analysis for the common elements the attempt is made to divide the elements here under consideration into two groups by treating the filtrate from the hydrogen sulfide precipitate first with ammonium hydroxide, and then filtering off the precipitate and treating the filtrate with ammonium sulfide. This plan was rejected by Noyes, Bray, and Spear in their earlier published system of analysis, because of the known inadequacy of the method in certain instances. They cited the complete precipitation of zinc with chromium, when the latter is present in larger proportion, and that of manganese when phosphate is present in excess; also the partial precipitation of manganese in all cases owing to its rapid oxidation by the oxygen of the air after the solution has been made alkaline. The ammonium hydroxide precipitation was, however, retained for separating aluminum from zinc, and for separating ferric iron from cobalt, nickel, and zinc. This was done without special investigation, since the processes are commonly employed even for quantitative purposes. The use of ammonium hydroxide for these and other separations has, however, since been studied in connection with this research; and the method has been found to be extremely unsatisfactory under the conditions commonly employed. Its use has therefore been avoided, so far as possible, throughout this system of analysis.

Some of the more important facts established in this investigation are briefly summarized here. The detailed results will be found among the Confirmatory Experiments (on D. 96).

A series of "precipitation experiments" was made by adding salts of two elements to 100 cc. of a cold solution 0.3 normal in hydrochloric acid; enough 15 normal ammonium hydroxide was added to give an excess of about 2 cc.; and the mixture was then heated to boiling, cooled, and filtered. The results are as follows:

Milligrams taken	Percent of the cobalt in ppt.	Milligrams taken	Percent of the zinc in ppt.
100 Ti, 2 or 20 Co	92–97	100 Ti, 2 or 20 Zn	75–80
200 Al, 2 or 20 Co	95–99	200 Al, 2 or 20 Zn	92
100 Zr, 2 or 20 Co	90–95	100 Zr, 2 or 20 Zn	50–70
200 Fe^{III}, 2 or 20 Co	97–99	100 Fe^{III}, 2 or 20 Zn	75
100 Th, 2 or 20 Co	50–70	100 Th, 2 or 20 Zn	25

In similar experiments with nickel, the proportion of it carried down was in each case nearly the same as that of the zinc, except that in the 20 mg. experiments a smaller proportion of the nickel (than of the zinc) was carried down by aluminum and ferric iron.

In another series, 20 mg. of zinc were present in each experiment with 50 mg. of each of various other elements; and the total volume was about 28 cc. The percentages of the zinc carried down by the hydroxides of the other elements named in the heading are as follows:

Ti	Al	Zr	Fe	Be
53	48	23	21	8

A series of "adsorption experiments" was also made in which an ammoniacal solution of cobalt was added to a suspension of freshly precipitated hydroxide of titanium or ferric iron; or one of zinc to a suspension of aluminum hydroxide. It was found that cobalt and zinc were adsorbed by the hydroxides, that the process was very rapid when the mixtures were heated, and that the proportion of the added elements adsorbed by the hydroxide approached that carried down in the "precipitation experiments." The results shown in the tables above therefore represent approximately the equilibrium distribution of the adsorbed element between precipitate and solution. The failure of certain attempts to improve the separation by adding an acid solution to excess of ammonium hydroxide is therefore not surprising. In spite of the stability of the ammonia complexes of cobalt and zinc, large proportions of these elements are adsorbed by highly dispersed hydroxide precipitates.

Recently, however, Ardagh with Broughall and with Bongard [1] has made the important discovery that the adsorption of nickel and zinc by ferric or aluminum hydroxide can be prevented. His method, which involves a radical change in the conditions, consists in evaporating an acid solution of the mixture to a very small volume, adding a large quantity of solid ammonium chloride and concentrated ammonium hydroxide, and stirring thoroughly. New experiments by this method have shown that the separation from iron is satisfactory also in the case of cobalt. These results

[1] Ardagh and Broughall, *Can. Chem. Metal.*, **7**, 198 (1923); Ardagh and Bongard, *J. Ind. Eng. Chem.*, **16**, 297 (1924).

are doubtless mainly due to the fact that the precipitated hydroxide is in a much less dispersed form than usual, and therefore has less adsorptive capacity. Also the high concentration of ammonium hydroxide increases the stability of the ammonia complexes, and must assist greatly in retaining in solution the nickel, zinc, or cobalt. The new process deserves extended study with reference to its further use in qualitative and quantitative analysis.

D. 97. Separation of Nickel, Cobalt, Zinc, and Indium from Other Elements by Hydrogen Sulfide in Acetate Solution.—An attempt was also made to isolate a group of elements (nickel, cobalt, zinc, indium) by passing hydrogen sulfide into the filtrate from the ammonium acetate precipitate after duly adjusting the concentration ratio of acetate-ion to acetic acid, and therefore the hydrogen-ion concentration. The separation of these elements from manganese and beryllium was satisfactory; but not from chromium. Moreover, uranium passed mainly into the precipitate or filtrate according to the conditions. For the results in detail see the Confirmatory Experiments on D. 97 and P. 123.

PRECIPITATION AND PARTIAL ISOLATION OF THE ALUMINUM, NICKEL, ZIRCONIUM, AND RARE-EARTH GROUPS

Tabular Outline IX

See page 148.

Procedures and Notes

Procedure 91.—*Detection of Iron and of Phosphate.*—Boil one twentieth of the filtrate from the H_2S precipitate (P. 71) till the H_2S is expelled, add to it 5 drops of 6 n. HNO_3, and evaporate it almost to dryness. Cool, and add to the residue 5 cc. of 6 n. HCl and 1 cc. of 12 n. HCl, and transfer the solution to a separating funnel. Add an equal volume of ether, and shake the mixture vigorously. When the layers have fully separated, draw off the water layer completely.

Evaporate the ether layer on a steam-bath. To the residue add ½ cc. of 6 n. HCl, 10 cc. of water, and 2 cc. of 1 n. KCNS. (Red color, presence of IRON.) To the mixture add 2 cc. of 6 n. NH_4OH, and heat the mixture to boiling. (Red precipitate, presence of IRON.)

Evaporate the aqueous layer almost to dryness. Add 3 cc. of water, pour the solution into a clear mixture of 5 cc. of 1 n. $(NH_4)_2MoO_4$ reagent and 5 cc. of 6 n. HNO_3, previously heated to about 70°; and let the mixture stand 5–15 minutes. (Yellow precipitate, presence of PHOSPHATE.)

Notes.—1. Iron is tested for here, since $Fe(NO_3)_3$ is to be added to the main solution in P. 92. Phosphate is also conveniently tested for at this point, since all of it that did not pass into the tungsten-tantalum group is present here.

2. The extraction with ether in the iron test serves to separate iron from all other elements likely to be present in the solution, so that the size of the NH_4OH precipitate enables the quantity of iron to be estimated. Over 95% of the iron is removed in a single extraction, provided the HCl concentration is about 7 normal. In regard to this extraction, see Note 3, P. 93.

3. The only other elements extracted by ether are gallium and trivalent thallium; and only the latter yields a red precipitate

with NH_4OH. Thallium should have been removed as TlBr in P. 61; and, even if present, it would not give a color with KCNS.

4. The precipitation of the yellow $(NH_4)_3PO_4(MoO_3)_{12}$ in the test for phosphate is more rapid and more complete when NH_4NO_3, $(NH_4)_2MoO_4$, and HNO_3 are present at high concentration, and when the mixture is warm. Heating above 70° is, however, to be avoided, since it may produce a precipitate of MoO_3 in the acidified reagent. Under the prescribed conditions 1/40 mg. of PO_4 can be detected in the 5-cc. portion, corresponding to ½ mg. of it in the whole solution.

Procedure 92.—*Partial Precipitation of the Elements by Ammonium Acetate.*—Boil the remainder of the filtrate * from the H_2S precipitate (P. 71) in a 300-cc. flask until the H_2S is expelled. Add liquid Br_2, a drop at a time, until a slight excess is present; then expel the excess by boiling. To the solution add just 4 cc. of 6 n. NH_4OH and (to the still acid solution) 15 cc. of neutral 3 n. $NH_4C_2H_3O_2$, and boil the mixture gently for 2 minutes. (No precipitate, absence of more than 2 mg. of IRON, ALUMINUM, GALLIUM, TITANIUM, and ZIRCONIUM.) Cool the mixture, add to it 3 n. $Fe(NO_3)_3$, 1 cc. at a time, till the mixture becomes red, and then 3 cc. more. Boil the mixture gently for 2 minutes, and let it stand a minute or two. (If the precipitate has not coagulated so as to leave a clear supernatant liquid, add 2.0 cc. of 6 n. NH_4OH, and boil again for 2 minutes. If the precipitate still has not coagulated, add 5 cc. of 1 n. $(NH_4)_2HPO_4$, and boil again for 2 minutes.) Filter the mixture with the aid of suction through an ordinary filter supported by a small hardened filter, keeping the mixture in the flask hot during the filtration. (If the first runnings of the filtrate have the brown shade characteristic of iron, pour the filtrate back into the flask, add to it just 1 cc. of 6 n. NH_4OH, test it with blue litmus paper, and, unless this is reddened, add 6 n. $HC_2H_3O_2$ to distinct acid reaction, and boil again for 2 minutes; repeating these operations, if necessary.) Wash the precipitate with hot water; and suck out the water.

Treat the precipitate by P. 93. Treat the filtrate by P. 96.

* For practice-analyses use a mixture of test-solutions of gallium, chromium, zirconium, and uranium (1 cc. of each) with 5 cc. of 6 n. HCl and 90 cc. of water. Treat the mixture by P. 92–96.

Notes.—1. Br_2 is added to the filtrate, after boiling out the H_2S, to oxidize the iron so that it may precipitate completely in the following treatment. Vanadyl salts are also oxidized to vanadic acid.

2. The hydrogen-ion concentration is then reduced to about 3×10^{-6} molal, by adding the proper amounts of 6 n. NH_4OH and 3 n. $NH_4C_2H_3O_2$, so as to permit iron to precipitate on boiling the solution. This is attained with the quantities prescribed in the procedure. Thus the solution submitted to the H_2S precipitation contained 30 milliequivalents of $HClO_4$ and HCl, and this is reduced to 6 milliequivalents of acid by the addition of 4 cc. of 6 n. NH_4OH; hence on adding 45 milliequivalents of $NH_4C_2H_3O_2$, the resulting solution contains 6 milliequivalents of free $HC_2H_3O_2$ and 39 of $C_2H_3O_2^-$ ion, the ratio being 1 : 6½, which ratio multiplied by the ionization-constant of acetic acid (2×10^{-5}) gives 3×10^{-6} for the H^+ concentration. Since about 10 milliequivalents of $Fe(NO_3)_3$ are added, the precipitation of this iron, even if thrown down wholly as $Fe(OH)_3$, would increase this ratio only to 16:29 (approximately 1 : 2); and at this acidity the iron still precipitates completely. When much aluminum is present, there results, owing to its very small equivalent weight, a much larger increase in acidity, which has to be compensated by the addition of NH_4OH.

3. The formation or non-formation of a precipitate on first heating the mixture to boiling is a useful indication of the presence or absence of certain elements. When present alone, the various elements behave as follows under the conditions of the procedure. Iron, aluminum, titanium, zirconium, and gallium, in excess of 1–2 mg., always give a precipitate; but large amounts, especially of aluminum, may not separate completely at this point. Other elements when present alone ordinarily remain wholly in solution, except that chromium or beryllium may yield a small precipitate. A considerable increase in the hydrogen-ion concentration may prevent the precipitation of those that otherwise come down; and a considerable decrease may cause other elements to precipitate, and gallium to dissolve.

4. The iron added to the solution as $Fe(NO_3)_3$ combines with any PO_4 present in the $HC_2H_3O_2$ solution to produce a precipitate of $FePO_4$, which is only slightly soluble in weakly acid solutions, thus preventing the precipitation of alkaline-earth elements as phosphates on the subsequent addition of NH_4OH. Since $FePO_4$ is light-yellow, an excess of iron is shown to have been added

when the mixture assumes a reddish color owing to the presence of colloidal $Fe(OH)_3$ (or basic ferric acetate), which is coagulated by the subsequent boiling. When phosphate is present with quadrivalent elements or with trivalent elements other than iron, such as the rare-earths, these elements may be precipitated in combination with the phosphate.

5. A moderate quantity (10 milliequivalents) of iron, in excess of any required to combine with PO_4, is added in order to carry down into the precipitate all the gallium, vanadium, and tungsten. For these elements should be removed here, since they would not be precipitated completely on the subsequent addition of NH_4OH and $(NH_4)_2S$. The iron also carries down chromium and indium (unless present in very large quantity) almost completely.

6. Little, if any, of the manganese is carried out by iron in the acetate treatment. The iron, moreover, carries down only a small part of the zinc, nickel, cobalt, uranium, and beryllium when much of these elements is present (thus about 20 mg. out of 200 mg. of zinc, nickel, or cobalt); and a considerable proportion remains in the filtrate even when only 1–2 mg. are present. Large quantities of titanium, zirconium, and chromium, present with the iron, do not materially increase the amounts of these elements carried into the precipitate (though this would not be the case if the solution were made alkaline by adding too much NH_4OH). For these reasons it is not necessary to test for nickel, cobalt, zinc, uranium, and beryllium in the analysis of the acetate precipitate; and in fact no provision is made for detecting nickel and cobalt in this precipitate. The quantities of zinc, uranium, and beryllium, as well as of any other aluminum-group element, which may divide between the acetate precipitate and filtrate, are later reunited in the filtrates from the Na_2O_2 treatments in P. 95 and 97.

7. When too much $HC_2H_3O_2$ is present, owing to improper adjustment of the acidity before the $NH_4C_2H_3O_2$ is added, or owing to the separation of a large hydroxide precipitate (especially of aluminum), the iron does not precipitate completely or does not coagulate well, but produces a dark-red colloidal solution or a brown turbid mixture. When this occurs, 2 cc. more of 6 n. NH_4OH are added and the mixture is boiled again. In case coagulation does not now result and the size of the precipitate indicates that the solution may be still too acid, a little more NH_4OH may be added, the solution being however tested with

litmus-paper to make sure that the solution remains acid. When a rare-earth element is present, the coagulation of the iron may not occur even under the prescribed condition of moderate acidity; but it can be brought about by addition of an amount of phosphate nearly equivalent to the rare-earth element, whereby the latter is largely or completely precipitated with the iron.

8. Short gentle boiling promotes the coagulation and settling of the precipitate, but long-continued or violent boiling may convert it into a finely divided suspension which filters very slowly. The solution is not allowed to cool before or during the filtration, and cold water is not used for the washing, since then some of the precipitate may redissolve.

Procedure 93.—*Dissolving of the Acetate Precipitate and Extraction of Iron and Gallium.*—Transfer the acetate precipitate (P. 92) to a casserole, add 5–10 cc. of 6 n. HCl, evaporate the mixture to about 1 cc., and add 10 cc. of 6 n. HCl. Without filtering, transfer the (cold) solution to a separating funnel, add an equal volume of ether (previously shaken with twice its volume of 6 n. HCl), shake vigorously several times, and then allow the two layers to separate. Draw off the water layer, preferably into a second separating funnel, and treat it with ether as before; if necessary, repeat this treatment once or twice until the ether layer remains colorless (see Note 4).

Treat the first two ether extracts by P. 94, rejecting any further extracts. Treat the HCl layer by P. 95.

Notes.—1. The hydroxides and most of the phosphates when freshly precipitated from the acetate solution dissolve readily in the HCl. If, however, titanium, zirconium, or thorium is present together with phosphate, or if a precipitate of their hydroxides has been allowed to stand a long time before treating it with acid or has been long heated during the acetate precipitation, these elements may remain in part undissolved even by the hot acid. For this reason the mixture is not filtered until after the treatment with NaOH and Na_2O_2 in P. 95.

2. The ether extraction removes from the HCl solution gallium and iron as $GaCl_3$ and $FeCl_3$. (It will also remove thallium as $TlCl_3$ if it has not been eliminated in P. 61.) This extraction is by far the simplest method of separating gallium from most of the other elements. If it were omitted, the gallium would pass

into the aluminum group and would divide in the $NaHCO_3$ treatment in P. 101. It is also advantageous to remove the iron before treating the solution with NaOH and Na_2O_2 (P. 95), since the size of the precipitate produced by these reagents is thereby diminished, thus decreasing the tendency to carry down zinc and other elements of the aluminum group. All elements except iron and gallium that may be present in the HCl solution remain in the aqueous layer. When much zirconium or tungsten is present a precipitate may form on the addition of ether; but this remains suspended in the water layer, together with any other substances undissolved by the HCl.

3. The extraction of $FeCl_3$ or $GaCl_3$ by ether depends on the concentration of HCl in the aqueous phase. The proportion of either salt that passes into the ether layer is less than 5% with 2 n. HCl, reaches a maximum in the neighborhood of 6 normal, and again becomes small at high concentrations (above 8 normal) as the two layers approach complete miscibility. In the case of gallium a maximum of 98% extraction is attained at about 5.5 n. HCl, and over 90% is removed within the concentration limits of 4.3–6.5 n. HCl. In the case of iron the corresponding values are approximately: a maximum of 99% at 6.0–6.4 n. HCl, and over 90% in the range of 5.5–7.5 n. HCl. Thus 90–98% of either element will be recovered if the HCl concentration is maintained between the rather narrow limits of 5.5–6.5 n. If the directions in the procedure are followed, the concentration is initially not above 6.5 n., and decreases during the operations to 6.0 n. or a little less. It is evident that after three extractions there will remain in the water layer not more than 0.1% of the iron or gallium originally present, and usually much less than this amount. Since the color of the ether layer is a sensitive indication of iron, the treatment with ether may be discontinued as soon as a nearly colorless ether extract is obtained. When titanium is present the water layer may remain distinctly yellow, owing to the presence of H_2O_2 as impurity in the ether; such a color does not, therefore, show that iron is still present.

4. As to the most suitable form of separating funnel, see Note 4, P. 51.

Procedure 94.—*Detection of Gallium.*—Evaporate the first two ether extracts (P. 93) on a steam-bath to 1 cc., add 10 cc. of 6 n. HCl, heat the mixture to about 70°, and pour it into a small flask. Add 0.5–1.0 cc. of metallic mercury, cork the

flask, shake the mixture vigorously for 5 minutes, keeping it at 60–80°. Cool it, and filter it at once into a separating funnel containing about 0.1 cc. of mercury and 10 cc. of ether previously shaken with 6 n. HCl. Wash the precipitate on the filter with 2–3 cc. of 6 n. HCl, collecting the washings in the separating funnel. Reject the precipitate (or test it for thallium, see Note 5). Shake the mixture in the separating funnel for half a minute, and then let the two layers separate.

Draw off the water layer; reject it (or test it for thallium, see Note 5).

Wash the ether layer in the separating funnel by adding 3 cc. of 6 n. HCl and 0.1 cc. of mercury, shaking the mixture, and drawing off and rejecting the water layer. Evaporate the ether extract just to dryness on a steam-bath, and add 5 cc. of water. To the solution add just 2 cc. of 6 n. NaOH, heat it to boiling, and cool it; add 15 cc. of water, and filter off and reject the precipitate. Add 6 n. $HC_2H_3O_2$ until the solution is just acid to litmus, and then add 1 cc. more. Dilute the mixture to 100 cc., boil it gently for 10 minutes, and let it cool. (White precipitate, presence of GALLIUM.)

Collect the precipitate on a small filter, dissolve it by pouring repeatedly through the filter a 3-cc. portion of 6 n. HCl, add 5 cc. of water and 3 cc. of 1 n. $K_4Fe(CN)_6$, and let the mixture stand 5–10 minutes. (White or bluish-white precipitate, presence of GALLIUM.)

Notes.—1. This separation of gallium from iron depends on the fact that $FeCl_2$, unlike $FeCl_3$, is scarcely at all extracted by ether from a 6 n. HCl solution. The $FeCl_3$ is almost completely reduced to $FeCl_2$ by metallic mercury in the presence of HCl, provided the mixture is vigorously shaken at 60–80° for 5 minutes. When the HCl concentration is 6 normal and the solution is shaken with an equal volume of ether, over 90% of the gallium passes into the ether layer, while almost all the $FeCl_2$ remains with the Hg and Hg_2Cl_2 in the aqueous layer. The ether layer is washed once with 6 n. HCl to remove the ferrous iron more completely. A little mercury is added during the final shaking, and the operations are carried out without interruption, so as to diminish the reoxidation of the $FeCl_2$ by the air.

2. In the treatment with NaOH the gallium remains in solution as sodium gallate, $NaGaO_2$, and the iron is precipitated as $Fe(OH)_3$. Such a treatment to remove the iron is necessary, since at best 0.1–0.2 mg. of iron always remains in the ether layer, and the amount may be much larger if the directions have not been followed, or if the ether contained H_2O_2 as is often the case.

3. The conditions for the precipitation of gallium from a boiling solution of $NaC_2H_3O_2$ and $HC_2H_3O_2$ are similar to those in P. 92. Under the conditions specified 1 mg. of gallium can be detected, but the test is less delicate if the H^+ concentration is either much greater or much less than that provided for. When the amount of gallium is very small, its presence is first indicated by the opalescence of the solution after a few minutes' boiling. This is followed by the formation of a finely divided precipitate, which slowly settles on standing. Frequently some of the precipitate is deposited on the glass as a firmly adhering film.

4. The precipitation of gallium as ferrocyanide is a delicate test in 1 n. to 2 n. HCl; 0.5 mg. giving a distinct turbidity within 2 minutes. The acid solution on standing becomes greenish-blue, more rapidly at higher acid concentrations; and the gallium ferrocyanide usually has a distinct bluish tint. This is due to the slow decomposition of $H_4Fe(CN)_6$. The confirmatory test serves to distinguish gallium from aluminum (introduced from the reagents or vessels), which would have remained with it in the NaOH solution and might have precipitated with it from the acetate solution. Zinc gives a similar precipitate with $K_4Fe(CN)_6$ in the acid solution, and iron a blue one; but these elements should have been completely removed in the preceding operations. (Gallium may be conveniently recovered from its ferrocyanide by adding the precipitate to 100 cc. of 0.1 n. NaOH, filtering if necessary, and passing CO_2 into the cold solution until it is saturated; for in this dilute slightly acid $NaHCO_3$ solution the gallium is completely precipitated free from ferrocyanide.)

5. Thallium can be present at this point only when it was not removed as TlBr by the HBr treatment in P. 61 (as in case of the solution from the fusions in P. 10 and 11). In P. 92 it would be oxidized to the trivalent state by the Br_2, and precipitated with the iron in the acetate treatment. It would then pass as $TlCl_3$ into the ether layer, and on shaking with Hg return to the 6 n. HCl solution because of its reduction to the univalent state. It may be tested for in this solution (which contains also $FeCl_2$) by adding to it 2–3 cc. of 1 n. KI, when its presence is shown by the forma-

tion of a yellow precipitate of TlI. Any thallium in excess of about 10 mg. remains as solid TlCl with the excess of Hg and the precipitated Hg_2Cl_2. The TlCl may be separated from these by pouring repeatedly through the filter a 15-cc. portion of hot water, and tested for thallium by adding 6 n. H_2SO_4 and 1 n. KI. See Note 1, P. 62; and Note 2, P. 63.

Procedure 95.—*Treatment of the Solution from the Acetate Precipitate with Sodium Peroxide.*—Evaporate the HCl solution (P. 93) to 1 cc.; add 2 cc. of 16 n. HNO_3, and evaporate the mixture almost to dryness. Add 10 cc. of water; and, without filtering, add 6 n. NaOH till the mixture is alkaline (see Note 6). Transfer it, if practicable, to a nickel or platinum dish (see Note 7), adding 10–20 cc. of water if the mixture is thick with precipitate. Place the dish in a vessel of cold water, and gradually sprinkle into the mixture from a dry 10-cc. graduate 1–3 cc. of Na_2O_2 powder, with constant stirring. Boil the mixture gently for 5 minutes, replacing the water that evaporates. Dilute the mixture to 40 cc., and heat it to boiling. (Precipitate, presence of ZIRCONIUM, TITANIUM, INDIUM, or RARE-EARTH ELEMENTS.) Cool the mixture, filter it through a hardened filter, using suction, and wash the precipitate thoroughly with hot water.

Analyze the filtrate for the aluminum group by P. 101–116, first uniting it with the filtrate that is obtained in P. 97.

Treat the precipitate by P. 131, uniting it with the NH_4OH precipitate that is obtained in P. 123.

Notes.—1. The HCl solution is evaporated to remove the excess of free acid. HNO_3 is added and the mixture is again evaporated to remove nearly all the chloride, which would otherwise give a precipitate of $PbCl_2$ in the subsequent test for chromate with $Pb(NO_3)_2$.

2. Of the elements which are completely or largely precipitated in the acetate treatment, zirconium, titanium, indium, thorium, and the rare-earth elements are precipitated by NaOH as white hydroxides which are left undissolved after the boiling with Na_2O_2 solution; while aluminum, chromium, vanadium, and tungsten are dissolved partially or completely by the moderate excess of cold NaOH, and are entirely dissolved by the treatment

with Na_2O_2. Of the elements that may be carried down in small or medium quantity into the acetate precipitate, cobalt, nickel, and manganese are precipitated as their bivalent hydroxides by the excess of NaOH, and are converted by the Na_2O_2 (incompletely in the case of nickel) into the still less soluble hydroxides corresponding to their higher valences; while zinc and beryllium are dissolved by the NaOH and are not then affected by the Na_2O_2; and uranium, though precipitated as sodium diuranate ($Na_2U_2O_7$) by NaOH, passes into solution as peroxyuranate on the addition of Na_2O_2. By the action of the boiling NaOH solution any phosphates, even those of zirconium, titanium, and thorium, are almost completely converted into hydroxides with the formation of Na_3PO_4 in the solution.

3. All the substances produced by the NaOH and Na_2O_2 treatment are white with the following exceptions. Cerium yields with Na_2O_2 yellow or orange $CeO_2 \cdot H_2O_2$. Chromium forms with NaOH a greyish-green precipitate of $Cr(OH)_3$ or a light-green solution of $NaCrO_2$, and is converted by the Na_2O_2 into Na_2CrO_4, whose yellow color is evident even with 1 mg. of chromium. Cobalt gives with NaOH a pink precipitate of $Co(OH)_2$ or a blue one of basic salt, which is changed by Na_2O_2 into black $Co(OH)_3$. Nickel yields with NaOH green $Ni(OH)_2$, which may be partially converted by Na_2O_2 into black $Ni(OH)_3$. Manganese forms at first white $Mn(OH)_2$, converted by the Na_2O_2 into brownish-black $MnO(OH)_2$. Uranium gives with NaOH a yellow precipitate of $Na_2U_2O_7$, which dissolves on adding Na_2O_2 to form a solution which is noticeably yellow with 1 or 2 mg. of uranium and red with 10 mg. or more.

4. Even a cold solution of Na_2O_2 decomposes with evolution of oxygen, and this decomposition takes place with violence when a large portion of the solid is added to a hot solution. It is best to transfer a little of it from the container directly (without using paper) to a dry 10-cc. graduate, and then to sprinkle it into the solution with constant stirring. A steady evolution of gas after the mixture has been well stirred is an indication that sufficient peroxide has been added. When much chromium is present, it should be added till the green precipitate disappears and the liquid assumes a deep-yellow color.

5. The mixture is boiled before dilution in order to destroy the excess of Na_2O_2 and to cause the precipitation of titanium, some of which at first passes into solution as the peroxytitanate. When only a small quantity of titanium is present here, as is

usually the case since ordinarily only about 4 mg. of this element pass into the filtrate from the tungsten-tantalum group (see Note 5, P. 6), substantially all of it is precipitated by five minutes' boiling of the mixture. When a large quantity of titanium is present, a few milligrams of it may still remain in solution. The solution is diluted and again boiled, so as to ensure the complete precipitation of $In(OH)_3$. The dilution also diminishes the disintegration of the filter-paper in the subsequent filtration, and a hardened filter is used for the same reason.

6. Since aluminum and silicon are very likely to be present in the NaOH reagent and may be present in the Na_2O_2 reagent, a blank test for these impurities should be made whenever new reagents are employed for the first time. This is done by acidifying with HCl 10 cc. of the 6 n. NaOH, or a solution of 2 g. of Na_2O_2 in 10 cc. of water, making the mixture slightly alkaline with 6 n. NH_4OH, adding to it 2 cc. of 3 n. NH_4Cl, heating it nearly to boiling, and comparing the precipitate with that given by 1 mg. of aluminum when precipitated from 20 cc. of 1 n. NH_4Cl by a few drops of 6 n. NH_4OH. It is also well at the same time to test for zinc by passing H_2S into the ammoniacal solution. If the NaOH available is found to contain considerable aluminum or silicon, it should not be used for neutralizing the acid at the beginning of this Procedure, but should be replaced by an additional quantity (0.5 cc. more) of Na_2O_2, which is usually much freer from impurities.

7. It is recommended to transfer the mixture to a nickel or platinum dish, since the alkaline solution during five minutes' boiling attacks a porcelain casserole to such an extent as to introduce 1–2 mg. of aluminum and silicon into the solution. A clean smooth nickel vessel is so little attacked by Na_2O_2 solution that not more than 0.05 mg. of this element is introduced; and even more than this could do no harm, since the precipitate resulting in this procedure is not tested for nickel. A platinum dish is entirely unacted upon. In case porcelain is used, the control tests with the reagents should include boiling the Na_2O_2 solution for five minutes in a casserole.

Procedure 96.—*Completion of the Precipitation of the Aluminum, Nickel, and Rare-Earth Groups by Ammonium Hydroxide and Sulfide.*—To the filtrate from the acetate precipitate (P. 92) add 6 n. NH_4OH, 1 cc. at a time, till the mixture after shaking smells of ammonia, then 2 cc. more; and heat

the mixture to boiling. (INDICATIONS, see Note 1.) Pass into the mixture a slow current of H_2S till after shaking its odor is perceptible; adding more 6 n. NH_4OH if the solution does not remain alkaline. Heat the mixture nearly to boiling. (INDICATIONS, see Note 2.) Filter the mixture through a hardened filter with the aid of suction, and wash the precipitate with (colorless) 0.06 n. $(NH_4)_2S$ solution; covering the funnel with a watch-glass. Boil the filtrate for half a minute, or longer if it is dark colored; and, if a precipitate other than sulfur separates, collect it on a filter, wash it, and unite it with the main one.

Treat the precipitate by P. 97.

Analyze the filtrate for the alkaline-earth and alkali groups by P. 151–170.

Notes.—1. The effect of the addition of NH_4OH alone is noted because it often gives useful indications as to what elements are present. Under the prescribed conditions, which provide for a small excess of NH_4OH in the presence of ammonium salts and for heating the solution, beryllium and rare-earth elements are completely precipitated as hydroxides, and any uranium in excess of 2 mg. separates as ammonium diuranate, $(NH_4)_2U_2O_7$; also there are precipitated as hydroxides any small quantities of aluminum, chromium, zirconium, and indium that were not precipitated in the acetate treatment. All of these precipitates are white, except $Cr(OH)_3$ which is greyish-green, and $(NH_4)_2U_2O_7$ which is yellow. Manganous salts are oxidized rapidly by the oxygen of the air with separation of a brown precipitate of hydrated Mn_2O_3 or MnO_2. Zinc, nickel, and cobalt, when present alone, are completely dissolved, except that some cobalt may precipitate when it is present in large quantity. The ammoniacal solution of nickel is blue; and that of cobalt is of a reddish color, which darkens rapidly on exposure to the air owing to oxidation. If a smaller excess of NH_4OH is used than is directed, some zinc and much of the cobalt may remain undissolved when large amounts of these elements are present. If, however, a much larger excess of NH_4OH is employed, a few milligrams of aluminum and chromium may be dissolved, the latter giving a pink solution.

2. The treatment with H_2S in the presence of NH_4OH precipitates ZnS, MnS, NiS, and CoS. It converts $(NH_4)_2U_2O_7$

slowly into UO_2S and into UO_2 and S, which are so much less soluble than the diuranate that 1 mg. of uranium gives a precipitate. NiS and CoS are black; UO_2S is reddish-black, and UO_2 is darker in shade; ZnS is white; and MnS is flesh-colored, but turns brown on standing in the air owing to oxidation to hydrated Mn_2O_3 or MnO_2.

3. Colorless $(NH)_2S$ may be used in place of H_2S; but it is less satisfactory, since it is likely to contain polysulfide, which may cause several milligrams of nickel to pass into the filtrate, giving to it a dark color. The mixture is heated in order to coagulate the precipitate. It is directed to wash with water containing a little $(NH_4)_2S$, and to keep the filter covered, in order to avoid the oxidation of the sulfides by the air, by which soluble sulfates may be formed. The filtrate is boiled for a few moments to ensure the complete precipitation of $Cr(OH)_3$, or longer to ensure that of NiS, whose presence is indicated by a brown or nearly black color of the filtrate. If NiS runs through the filter during the washing, it may be removed from the wash-water by boiling.

4. If the directions given in the Procedure are followed, less than 0.5 mg. of any element of the nickel and rare-earth groups remains in solution.

Procedure 97.—*Dissolving of the Ammonium Sulfide Precipitate and Treatment of the Solution with Sodium Peroxide.*—To the $(NH_4)_2S$ precipitate (P. 96) in a casserole add 5–10 cc. of 1 n. HNO_3, stir the (cold) mixture for a minute or two, and heat it to boiling. If there is a black residue, add 1–3 cc. of 16 n. HNO_3, and heat the mixture till the residue becomes light-colored. Filter out any sulfur, and evaporate the solution to 1 cc. Add 10 cc. of water; and, without filtering, add 6 n. NaOH till the mixture is alkaline, then 1–2 cc. more (see Note 6, P. 95). Transfer it to a platinum dish, if one is available (see Note 5). Add 10–20 cc. more water if the mixture becomes thick with precipitate. Place the dish or casserole in a vessel of cold water, and gradually sprinkle into the mixture from a dry 10-cc. graduate 1–3 cc. of Na_2O_2 powder, with constant stirring. Boil the mixture gently for 2–3 minutes, dilute it to about 40 cc., and heat it to boiling. (Precipitate, presence of MANGANESE, NICKEL, COBALT, or RARE-EARTH ELEMENTS.)

Cool the mixture, filter it through a hardened filter, using suction, and wash the precipitate thoroughly with hot water.

Treat the filtrate by P. 101, first uniting it with the filtrate from P. 95.

Treat the precipitate by P. 121.

Notes.—1. The treatment with cold 1 n. HNO_3 rapidly dissolves all the hydroxides and sulfides except NiS and CoS, which are only slowly attacked. This weak acid is used at first so as to avoid the formation of sulfur and H_2SO_4, which latter interferes with the subsequent test for chromium with $Pb(NO_3)_2$. The mixture is then heated, if need be, with more concentrated acid to dissolve the NiS and CoS.

2. The elements which may be present here wholly or in large part are manganese, cobalt, nickel, zinc, uranium, beryllium, and rare-earths. Much aluminum and chromium may also be present if the hydrogen-ion concentration became large in the acetate precipitation.

3. For a discussion of the Na_2O_2 treatment and the behavior of all these elements in it, see Notes 2–5, P. 95. Since titanium is not present here, it is not necessary to boil the mixture for more than 2 or 3 minutes, since this suffices to decompose the free Na_2O_2. Moreover, longer boiling is not advisable; for it may cause gradual precipitation of uranium as $Na_2U_2O_7$ when much is present, owing to slow decomposition of the peroxyuranate.

4. This separation with NaOH and Na_2O_2 is a satisfactory one, except in the case of zinc. As much as 5 mg. of this element is almost completely carried down in the precipitate when much nickel or cobalt is present; and as much as 20 mg. of it may be completely precipitated when much manganese is also present. Provision is therefore made for the detection of zinc in the precipitate, as well as in the filtrate.

5. Since porcelain is considerably attacked by the boiling alkaline solution (see Note 7, P. 95), it is preferable to transfer the mixture to a platinum dish, which is unacted upon. It is not recommended to use a nickel vessel here (as in P. 95), since the precipitate is to be tested for nickel; however, the amount of nickel that is introduced from a clean smooth dish is very small.

6. The precipitate is collected on a hardened filter, so that paper may not be introduced on later dissolving it in HNO_3; for the presence of paper fiber may prevent the precipitation of manganese in the subsequent treatment with $KClO_3$.

Tabular Outline X

Analysis of the Aluminum Group

Filtrate from the Na_2O_2 treatments (P. 95 and 97): Cr, U, V, W, PO_4, Al, Zn, Be, as sodium salts (U as $UO_4.2Na_2O_2$).
Neutralize with HNO_3, add $NaHCO_3$ and H_2O_2, heat in closed bottle (P. 101).

Filtrate: Cr, U, V, W, PO_4, as Na_2CrO_4, $Na_4UO_2(CO_3)_3$, Na_3VO_4, Na_2WO_4, Na_3PO_4.
Add HNO_3 and $Pb(NO_3)_2$ (P. 102).

Precipitate, yellow: $PbCrO_4$.
Add HNO_3, ether, H_2O_2 (P. 103).

Ether layer, blue: H_3CrO_7.

Filtrate: $UO_2(NO_3)_2$, H_3VO_4, $H_3PO_4(WO_3)_{12}$, $Pb(NO_3)_2$.
Pass in H_2S, filter out the PbS, boil, add Br_2 (to oxidize V^{IV}) (P. 102). Neutralize, add $HC_2H_3O_2$ and Na_2HPO_4 (P. 104).

Precipitate: $UO_2NH_4PO_4$.
Dissolve in HCl, evaporate, add $K_4Fe(CN)_6$ (P. 105).

Precipitate, dark-red: $K_2(UO_2)Fe(CN)_6$.

Filtrate: H_3VO_4, $H_3PO_4(WO_3)_{12}$.
Add NH_4OH, saturate with H_2S (P. 106).

Solution: $(NH_4)_3VS_4$ (violet-red), $(NH_4)_2WS_4$.
Acidify with HNO_3 (P. 106).

Precipitate: V_2S_{4-5}.
Add HNO_3 and H_2O_2 (P. 106).

Solution, orange-red: peroxyvanadic acid.

Filtrate: $H_3PO_4(WO_3)_{12}$, $VO(NO_3)_2$.
Remove PO_4 with $Mg(NO_3)_2$ and NH_4OH, evaporate, add HNO_3 (P. 107).

Residue: H_2WO_4.
Confirm by P. 36.

Precipitate: Al, Zn, Be, as $Al(OH)_3$, $ZnCO_3$, $BeCO_3$. U and V as uranyl vanadate; ‡U with Al
Dissolve in HCl, add ether, saturate with HCl gas (P. 111).

Precipitate: $AlCl_3.6H_2O$.
Add HNO_3, $Co(NO_3)_2$, NH_4OH, filter, ignite (P. 112).

Residue, blue: $Al_2O_3.xCoO$.

Filtrate: $ZnCl_2$, $BeCl_2$, UO_2Cl_2, $VOCl_2$.
Evaporate, add water and NH_4OH (P. 113).

Filtrate: $Zn(NH_3)_4Cl_2$.
Add $HC_2H_3O_2$, H_2S (P. 114).

Precipitate, white: ZnS.
Dissolve in HNO_3, add $Co(NO_3)_2$ and Na_2CO_3, ignite (P. 114).

Residue, green: ZnO.xCoO.

Precipitate: $Be(OH)_2$, $(NH_4)_2U_2O_7$; also V, Al, Fe, †Zn.
Dissolve in $HC_2H_3O_2$, evaporate, add $CHCl_3$ (P. 115).

Solution: $BeO.3Be(C_2H_3O_2)_2$.
Evaporate, dissolve in HNO_3, add NH_4OH (P. 115).

Precipitate, white: $Be(OH)_2$.

Residue: U, V; Al, Fe, Zn, †Be.
Heat with $NaHCO_3$ (P. 116).

Solution: U, V.
Test for uranium. (P. 116, 105).

Residue: Al, Fe, Zn, Be.
Reject.

† ‡ For the significance of these signs see page 9.

ANALYSIS OF THE ALUMINUM GROUP

Tabular Outline X

See page 170.

General Discussion

D. 101. Primary Separation of the Elements by Sodium Hydrocarbonate (P. 101).—For the analysis of this group the process worked out by Noyes, Bray, and Spear [1] has been adopted with certain modifications and additions. The first step in this process consists in separating the elements into two subgroups by diluting the solution to 100 cc., adding to it 1.5 grams of sodium hydrocarbonate, and heating it to 100° in a closed bottle (to prevent loss of carbon dioxide). This produces such a hydrogen-ion concentration that aluminum, zinc, and beryllium are precipitated, while chromium, uranium, vanadium, and tungsten, which are present as anions, remain in solution as sodium salts. This separation is a satisfactory one, except in the following respects. A small quantity of uranium may be carried down almost completely when much aluminum is present, making it necessary to test for uranium in the precipitate as well as the filtrate. Moreover, when uranium and vanadium are simultaneously present, each in large quantity (such as 100 mg.), some uranyl vanadate precipitates; but, since a large proportion of the vanadium remains in solution, vanadium need be tested for only in the filtrate.

D. 102. Separation of Chromium, Uranium, Vanadium, and Tungsten from One Another (P. 102–107).—For the analysis of the filtrate from the hydrocarbonate precipitate the process devised by Noyes, Bray, and Spear has been adopted without essential modification. The process requires little comment. It may be mentioned, however, that provision is now made for the detection of tungsten, which will be found in this solution when it was originally present together with phosphate, since it is then not precipitated in the perchloric acid treatment (in P. 6). In the analysis of this group the tungsten remains with the vanadium

[1] Noyes, Bray, and Spear, *J. Am. Chem. Soc.*, 30, 485, 493, 502–511 (1908).

until the ammonium sulfide solution is acidified, whereupon the vanadium is largely, though not completely, precipitated, while the tungsten, because of the large quantity of phosphate present, remains in solution. In this solution it is detected, after removing the phosphate with magnesium nitrate and ammonium hydroxide, by precipitating it as tungstic acid with nitric acid; and it is then confirmed by the blue-color test with stannous chloride.

D. 103. Separation of the Aluminum, Beryllium, and Zinc Contained in the Hydrocarbonate Precipitate (P. 111, 113, 114).—In the scheme of Noyes, Bray, and Spear the precipitate produced by the hydrocarbonate treatment is analyzed by separating the zinc from the aluminum and beryllium by means of ammonium hydroxide, and then separating these last two elements from each other by Havens' method, which consists in precipitating the aluminum as aluminum chloride hexahydrate by adding ether to the solution and saturating it with hydrogen chloride gas. Since it has been found (as stated in D. 96) that the ammonium hydroxide separation of zinc and aluminum is very imperfect, these two operations are employed in the reverse order in this revised scheme of analysis. By proceeding in this way ammonium hydroxide is used only for the separation of zinc from beryllium (and uranium), for which it is fairly satisfactory. Thus not more than ten percent of 2 mg. or 20 mg. of zinc is carried out by 50 mg. of beryllium. From the ammoniacal filtrate, after acidification with acetic acid, the zinc is precipitated by hydrogen sulfide.

D. 104. Separation of Beryllium by Means of its Basic Acetate (P. 115).—Another marked improvement of the original process of Noyes, Bray, and Spear consists in the introduction of a more satisfactory method for separating beryllium from uranium and other elements that may accompany it in the final ammonium hydroxide precipitate, thereby increasing the reliability of its detection. Namely, the method which Haber and van Oordt[1] used for preparing pure basic beryllium acetate, $BeO \cdot 3Be(C_2H_3O_2)_2$, has been found to be well suited for this purpose. The process here employed consists simply in dissolving the ammonium hydroxide precipitate in acetic acid, evaporating this solution, re-

[1] Haber and van Oordt, *Z. anorg. Chem.*, 40, 465 (1904).

peating the evaporation with anhydrous acetic acid, treating the residue with chloroform, and washing the chloroform solution with a little water. The chloroform dissolves the basic beryllium acetate, but leaves behind aluminum, uranium, vanadium, titanium, and iron. The chloroform dissolves zinc to some extent, but it is removed by the washing with water. In the chloroform layer is therefore left only the beryllium, which can now be reliably tested for by precipitating it by ammonium hydroxide from nitric acid solution.

D. 105. Detection of Uranium (*P. 116*).—Since the residue from the chloroform treatment may under certain circumstances (see D. 101) contain nearly all the uranium that was in the material analyzed, it is examined for this element by removing any small quantities of aluminum, iron, zinc, and beryllium that may be present by a second sodium hydrocarbonate treatment, precipitating the uranium from the acidified filtrate by ammonium hydroxide, and then testing for it with potassium ferrocyanide.

MODIFICATION OF THE PROCESS INVESTIGATED

D. 106. Separation of Beryllium from Uranium by Precipitation in Presence of Hydroxylamine.—The method of Brinton and Ellestad [1] for the separation of beryllium and uranium was also investigated. Their method depends on the precipitation of beryllium by ammonium hydroxide or by boiling ammonium carbonate in the presence of hydroxylamine, which in sufficient amount prevents the precipitation of the uranium. When only a little beryllium is present, it is precipitated by ammonium hydroxide from a solution containing hydroxylamine. When much beryllium is present, nearly all of it is first precipitated as basic carbonate by boiling an ammonium carbonate solution to which hydroxylamine has been added, filtering, and, after acidifying and boiling the filtrate, precipitating from it the remainder of the beryllium with ammonium hydroxide; these two steps being necessary, since much more uranium is retained by the bulky gelatinous hydroxide precipitate than by the less dispersed basic carbonate. Their method was found by us to give a satisfactory separation of beryllium from uranium, even when vanadium is present.

[1] Brinton and Ellestad, *J. Am. Chem. Soc.*, 45, 395 (1923).

Any iron or aluminum present precipitates completely with the beryllium; but titanium divides between the precipitate and solution. The method was considered less satisfactory for the present purpose than the one adopted, since it will not give in all cases a pure compound of either beryllium or uranium.

ANALYSIS OF THE ALUMINUM GROUP

Tabular Outline X

See page 170.

Procedures and Notes

Procedure 101.—*Separation of Chromium, Uranium, Vanadium, and Tungsten from Aluminum, Zinc, and Beryllium.* —To the combined filtrates * from the Na_2O_2 precipitates (P. 95 and 97) add 6 n. HNO_3 (free from HNO_2), 0.5–1.0 cc. at a time, keeping the solution cool, until it reacts acid and remains so after shaking. Dilute the solution to 100 cc., and transfer it to a 125–200 cc. pyrex bottle. Add solid $NaHCO_3$, a little at a time, until the mixture after shaking no longer turns litmus-paper red at once; finally add 1.5 g. of solid $NaHCO_3$ (weighed out roughly), and 1 cc. of 1 f. H_2O_2. Close the bottle with a rubber stopper held securely in place by wiring it to the neck of the bottle or by clamping it in a pressure-bottle frame, place it in a vessel of warm water, and boil the water gently for 20 to 30 minutes. Cool the bottle to at least 50° (by slowly adding cold water to the bath), filter at once, and wash the precipitate thoroughly, using suction if it is large.

Treat the filtrate by P. 102. Treat the precipitate by P. 111.

Notes.—1. The alkaline solution is kept cold during the neutralization and much excess of HNO_3 is avoided because chromate in the presence of H_2O_2 and an acid is rapidly reduced to a chromic salt, especially when the solution is hot. This reduction, if complete, would prevent the detection of chromium in the subsequent test. Some H_2O_2 will, to be sure, be formed on acidification when uranium or titanium is present (see Note 3, P. 97, and Note 5, P. 95). Chromate would also be reduced if the HNO_3 contained HNO_2. The latter should therefore be previously removed from the 6 n. HNO_3 by boiling it one minute in an

* For practice-analyses use a solution made as follows. Mix in a casserole test-solutions of chromium (as nitrate), uranium, vanadium, aluminum, zinc, and beryllium (1 cc. of each); dilute the mixture to 20 cc.; add to it very gradually 2 cc. of Na_2O_2 powder; boil it gently for five minutes; dilute it to 40 cc.; and filter out any precipitate. Omit P. 107 and P. 116.

open vessel. To reoxidize the chromium that may be reduced a little H_2O_2 is added after the $NaHCO_3$; but this oxidation may not be complete since the H_2O_2 is rapidly decomposed in the hot mixture, especially when chromium is present.

2. The $NaHCO_3$ separation depends primarily on the fact that this salt in the presence of H_2CO_3 yields such a H^+ concentration that aluminum, zinc, and beryllium are precipitated. The carbonate also has a specific effect in causing the zinc to precipitate completely and a large quantity of uranium to remain in solution (as a sodium salt of a complex uranylcarbonic acid, probably $Na_4UO_2(CO_3)_3$). It would also dissolve some beryllium for the same reason, if used at too high concentration.

3. Since the $NaHCO_3$ may at first be used up in precipitating zinc, aluminum, and beryllium as well as in neutralizing the free acid, the weighed amount of $NaHCO_3$ is added only after the solution ceases to react distinctly acid. A much larger concentration of $NaHCO_3$ than 1.5% would not prevent the complete precipitation of zinc or of aluminum, but it would interfere with that of beryllium. Thus with a volume of 100 cc. the precipitation of the beryllium is complete when the $NaHCO_3$ content is 1%, and 1 mg. can usually be detected when it is 2%; but 3, 5, and 10% solutions dissolve about 3 mg., 15 mg., and 150 mg., respectively. A smaller concentration of $NaHCO_3$ and a smaller volume than 100 cc. are avoided, in order to prevent as far as possible the precipitation of uranyl vanadate, which may occur when large quantities (more than 100 mg.) of uranium and vanadium are simultaneously present (in 100 cc. of solution). The amount of vanadium that can be thus precipitated as uranyl vanadate is only a small fraction of the total amount of vanadium present at this point; and vanadium therefore need not be tested for in the precipitate. The presence of phosphate does not cause the precipitation of uranium, nor otherwise interfere with the analysis. When a large amount of aluminum or beryllium is present, 2 to 5 mg. of uranium may be carried down almost completely in the $NaHCO_3$ precipitate, so that in this case uranium has to be tested for in the analysis of the precipitate.

4. Of any titanium that may have remained in solution in the Na_2O_2 treatment, owing to incomplete decomposition of the peroxytitanate (Note 5, P. 95), all in excess of 0.3–0.5 mg. passes into the $NaHCO_3$ precipitate. If gallium were not removed by the ether extraction in P. 93, it would, if more than 20 mg. were present, be divided between the precipitate and filtrate in this $NaHCO_3$ treatment.

Procedure 102.—*Separation of Chromium from Uranium and Vanadium.*—To the cold filtrate from the $NaHCO_3$ precipitate (P. 101) add 6 n. HNO_3 (free from HNO_2), 0.5–1.0 cc. at a time, till the mixture reddens litmus paper. (Perfectly colorless solution, absence of CHROMIUM.)

In case the solution is as colorless as water, add 3 cc. of 6 n. HNO_3, and treat it by P. 104.

In case the solution is at all yellow, exactly neutralize the HNO_3 solution with 6 n. NaOH, add 2 cc. of 6 n. HNO_3 and then 25 cc. of 1 n. $Pb(NO_3)_2$; allow the mixture to stand for 15 to 20 minutes, and filter it. (Yellow precipitate, presence of CHROMIUM.) Wash the precipitate and treat it by P. 103.

Saturate the filtrate with H_2S, filter off and reject the precipitate; boil the filtrate till the H_2S is expelled, cool it to 50°–60°, and add liquid Br_2, a drop at a time, till after waiting a minute or two an excess is still present. Boil the solution till the Br_2 is expelled, filter it if turbid, and treat it by P. 104.

Notes.—1. The precautions of keeping the solution cold during neutralization and avoiding much excess of HNO_3 (see Note 1, P. 101) are again observed, since some H_2O_2 may still be present.

2. If the acid solution is perfectly colorless, an amount of chromium exceeding 0.5 mg. may safely be pronounced absent. Uranium and especially vanadium in moderate quantity (20 to 50 mg.) also give yellow solutions.

3. The separation of chromium from vanadium and uranium by $Pb(NO_3)_2$ depends on the relatively small solubility of $PbCrO_4$ in dilute HNO_3 in the presence of a large quantity of $Pb(NO_3)_2$. Under the conditions described in the Procedure, over 100 mg. of vanadium yield no precipitate and only 0.1 to 0.3 mg. of chromium usually remains in solution, though this amount is somewhat increased when a very large quantity of $NaNO_3$ has been introduced. To secure these results, however, care must be taken to use the prescribed quantities of HNO_3 and $Pb(NO_3)_2$; for with more HNO_3 the chromium test is not delicate, and with less HNO_3 (yellow) lead vanadate might precipitate.

4. The presence of sulfate or much chloride or phosphate produces a white precipitate of the corresponding lead salt, which lessens the yellow color of a small quantity of $PbCrO_4$ and prevents the estimation of the amount of chromium present. Sulfate and chloride will, however, not be present in harmful quantity, if

in dissolving the $(NH_4)_2S$ precipitate (P. 97) the acids are used in the way prescribed, and if, in acidifying the solutions in P. 101 and 102, HNO_3 and not HCl is used, as directed.

5. The lead which is added to precipitate the chromate must be removed before testing for uranium with Na_2HPO_4 (in P. 104), since it would give a precipitate of $Pb_3(PO_4)_2$. It is precipitated with H_2S, rather than with $(NH_4)_2SO_4$, because with the latter reagent enough lead (about 1 mg.) still remains in solution to give a precipitate with Na_2HPO_4.

6. By the H_2S vanadic acid, H_3VO_4, is reduced to vanadyl nitrate, $VO(NO_3)_2$, slowly in the cold, but more rapidly on heating the solution, so that sulfur may be precipitated on boiling the filtrate to expel H_2S. The vanadyl salt is reoxidized to H_3VO_4 by adding Br_2; for otherwise $VONH_4PO_4$ would precipitate with the $UO_2NH_4PO_4$ in P. 104. Since the oxidation does not take place instantaneously, an excess of Br_2 is used, and the hot mixture is allowed to stand for a minute or two.

Procedure 103.—*Confirmation of Chromium.*—Pour repeatedly through the filter containing the $Pb(NO_3)_2$ precipitate (P. 102) a warm mixture of 2 cc. of 6 n. HNO_3 (free from HNO_2) with 8 cc. of water.

In case the solution is yellow, cool it, add to it in a test-tube 10 cc. of water, about 2 cc. of ether, and 0.3–1.0 cc. of 1 f. H_2O_2, and shake the mixture gently. (Blue coloration of ether layer, presence of CHROMIUM.) If the blue color fades and the aqueous layer is still yellow, add more 1 f. H_2O_2.

In case the solution is nearly colorless and the precipitate is still distinctly yellow, heat the precipitate with 15–30 cc. of 3 n. $NH_4C_2H_3O_2$, cool the mixture, filter it, and reject the filtrate. Now treat the precipitate again as described in this Procedure, using the same portion of HNO_3 as before.

Notes.—1. The blue compound which is formed by the action of H_2O_2 on chromic acid is one of the peroxychromic acids, and has the formula H_3CrO_7. It is a very unstable substance; by its decomposition oxygen is evolved and the chromium is reduced to the trivalent state. Its decomposition is greatly accelerated by an excess of H_2O_2, by the presence of much acid, and by raising the temperature; it is therefore important not to add too much H_2O_2, and to use cold dilute acid, as directed in the Procedure. On the other hand, when too little H_2O_2 is added and the chromic

acid is present in excess, the blue color either is not obtained or disappears when the mixture is shaken; in this case more H_2O_2 must be added. Under proper conditions 0.2 mg. of chromium may be detected, but the test may fail with a much larger amount if the directions are not followed.

2. In dissolving the $PbCrO_4$ the precipitate and filter are not heated with HNO_3 in a casserole, since reduction of the chromate by the paper is then more likely to occur. If in the procedure a green solution is obtained, the chromium must be reoxidized with Na_2O_2 in alkaline solution before making the test.

3. When a small amount of $PbCrO_4$ and a large amount of $PbSO_4$ are precipitated together in P. 102, the precipitate has a distinct yellow color; but the $PbCrO_4$ may then not be appreciably dissolved by 1.2 n. HNO_3. The treatment with 3 n. $NH_4C_2H_3O_2$ described in the last paragraph of the Procedure extracts a large part of the $PbSO_4$; but dissolves very little $PbCrO_4$. To lessen the amount of the $PbCrO_4$ dissolved, the $NH_4C_2H_3O_2$ solution is cooled and refiltered before rejecting it. The $PbCrO_4$ now dissolves to a large extent in 1.2 n. HNO_3. $Pb_3(PO_4)_2$, unlike $PbSO_4$, does not prevent $PbCrO_4$ from dissolving in the 1.2 n. HNO_3.

Procedure 104.—*Separation of Uranium from Vanadium.*—Evaporate the HNO_3 solution obtained in P. 102 to a volume of about 40 cc., and cool it. Make it neutral with 6 n. NH_4OH, add 5 cc. of 6 n. $HC_2H_3O_2$ and 15 cc. of 1 n. Na_2HPO_4, and heat the mixture to boiling. (White precipitate, presence of URANIUM.) Let the mixture stand 10 or 15 minutes to coagulate the precipitate, filter, and wash the precipitate with 1 n. NH_4NO_3.

Treat the precipitate by P. 105, and the solution by P. 106.

Notes.—1. The precipitation of white uranyl ammonium phosphate, $UO_2NH_4PO_4$, is a delicate test provided the solution be made only moderately acid with $HC_2H_3O_2$ and a sufficient excess of Na_2HPO_4 be added. The separation from quinquivalent vanadium is a very satisfactory one; for vanadium, even when present in large quantity (100 mg.), does not precipitate, nor is a small quantity carried down by uranium; on the other hand 0.3 mg. of uranium gives a distinct precipitate. The evaporation is advantageous, since the test is somewhat less delicate if made with the same quantities of reagents in the larger volume (100–125 cc.)

originally present. Moreover, it improves the subsequent test for vanadium (in P. 106); and is essential when tungsten is to be tested for (in P. 107).

2. The formation of a precipitate at this point is not sufficient evidence of the presence of uranium; for aluminum, beryllium, titanium, and lead separate as phosphates if they have not been completely removed in previous procedures, and vanadium may precipitate as $VONH_4PO_4$ if the oxidation by Br_2 was incomplete. On the other hand, a slight turbidity may correspond to an appreciable amount of uranium (0.2 to 0.5 mg.). Therefore, the confirmatory test for uranium (P. 105) should always be tried.

3. When the solution is made alkaline with NH_4OH a pale yellow precipitate of uranyl ammonium vanadate, $UO_2NH_4VO_4$, may separate, and may not dissolve when the $HC_2H_3O_2$ is added. This, however, has no effect on the separation, since on boiling it is converted into the less soluble $UO_2NH_4PO_4$ and vanadic acid.

4. In the absence of ammonium salts uranium is precipitated as UO_2HPO_4, which often separates as a very fine precipitate that runs through the filter. However, ammonium salts will always be present if HNO_3 was added in P. 102, as directed; and the uranium will then precipitate as $UO_2NH_4PO_4$, which coagulates and filters more readily.

Procedure 105.—*Confirmation of Uranium.*—Dissolve the Na_2HPO_4 precipitate (P. 104) or the NH_4OH precipitate (P. 116) by pouring a small portion of hot 6 n. HCl repeatedly through the filter, evaporate the solution until only about 0.2 cc. of liquid remains, add about 10 cc. of 5 n. NaCl, pour the mixture into a test-tube, cool it, add 5 cc. of 1 n. $K_4Fe(CN)_6$, and let it stand for 15 minutes. (Dark-red precipitate or coloration, presence of URANIUM.)

Notes.—1. The formation of the dark-red uranyl ferrocyanide, $K_2(UO_2)Fe(CN)_6$, is a characteristic test for uranium. The test is very delicate, provided a high concentration of ferrocyanide is used, and care has been taken to evaporate off nearly all the acid. The solution must, nevertheless, be distinctly acid; for otherwise uranyl ferrocyanide may not form, owing to the small concentration of uranyl ion, UO_2^{++}. It tends to form a colloidal solution, but the presence of NaCl and HCl soon causes it to coagulate,

when the amount of uranium is as large as 0.5 mg. Even 0.1 mg. of uranium gives a red color within 2–5 minutes if the acid present does not exceed 5 milliequivalents.

2. Vanadium, which may be present here (see Note 2, P. 104, and Note 1, P. 116), gives a greenish-yellow precipitate which can not be mistaken for the red uranium precipitate, and does not mask the color of even a small quantity of uranium. Titanium, in excess of 0.5 mg., gives with ferrocyanide in less than fifteen minutes a slowly settling, orange-yellow precipitate; but this amount cannot be present at this point (see Note 4, P. 101, and Note 2, P. 116). With a smaller quantity there is an orange-yellow color which does not obscure the uranium test. Beryllium in small quantity (up to about 20 mg.) gives no precipitate with the ferrocyanide.

Procedure 106.—*Detection of Vanadium.*—Neutralize the filtrate from the Na_2HPO_4 precipitate (P. 104) with 15 n. NH_4OH, and add 5 cc. more. Saturate the solution completely with H_2S by passing the gas through it in a small flask for 10 or 15 minutes. (Pink or violet-red color, presence of VANADIUM.) To the solution add gradually 6 n. HNO_3 (about 15 cc.) till it is distinctly acid, and heat the mixture nearly to boiling. (Dark precipitate, presence of VANADIUM.) Filter, and wash the precipitate.

Treat the filtrate by P. 107 in case phosphate was found in P. 91; otherwise reject it.

Heat the precipitate with 1–2 cc. of 16 n. HNO_3, add 3 cc. of water, and if there is a residue, heat the mixture to boiling. Cool, and add 1 cc. of 1 f. H_2O_2. (Orange-red color, presence of VANADIUM.)

Evaporate the solution just to dryness. Add 5 cc. of 1 n. NH_4OH, filter out any residue, and evaporate the filtrate just to dryness. Add 1–2 cc. of 1 n. NH_4OH completely saturated with NH_4Cl, pour the mixture into a test-tube, and let it stand for some hours, stirring it occasionally with a glass rod. If there is a precipitate, add to the solution one third its volume of water. (White crystalline precipitate remaining after addition of water, presence of VANADIUM.)

Notes.—1. All the vanadium present in the original material will usually be found in this Procedure; but it may sometimes be carried into the precipitate of the tungsten and tantalum groups, especially when tin is present (see Note 6, P. 6). It is then detected in P. 39 and 44.

2. An ammoniacal solution of a vanadate (or hypovanadate) quickly becomes yellowish-red when H_2S is led into it, and this color slowly deepens as more H_2S is absorbed; but the characteristic brilliant violet-red color is obtained only when the solution is completely saturated with H_2S. The presence of ammonium salts tends to prevent the formation of this red compound, but their influence is overcome by the addition of a large excess of NH_4OH. These facts make it probable that this red compound is an ammonium thiovanadate, such as $(NH_4)_3VS_4$. Under the conditions of this Procedure 0.1–0.2 mg. of vanadium can be detected, the solution then having a pink color. When much vanadium is present, some of it may separate as a brown precipitate; but this does not obscure the violet-red color.

3. Upon the addition of acid the thiovanadate is immediately decomposed, with formation of a black precipitate of V_2S_4 or V_2S_5. This precipitation is far from complete under these conditions, but more than half of the vanadium is always thrown down. Some sulfur will also be precipitated; but the dark color of the sulfide is apparent even with less than 0.5 mg. of vanadium.

4. If molybdenum were present in the solution, the saturation with H_2S would give a red color which would obscure the test for vanadium and might be mistaken for it, and on the addition of acid to the thiomolybdate solution a black precipitate of MoS_3 would form; but the confirmatory tests would distinguish it from vanadium. However, molybdenum should have been completely precipitated by H_2S in acid solution in P. 71.

5. Tungsten gives no color when the NH_4OH solution is saturated with H_2S, and in the presence of phosphate gives no precipitate (of WS_3 or H_2WO_4) on the addition of acid. The probability of the precipitation of black WS_3 would be greatly increased if the $(NH_4)_2S$ solution were poured into excess of acid, instead of being slightly acidified by adding the acid to it; but even then the presence of much phosphate almost completely prevents the precipitation of tungsten (see Note 2, P. 31).

6. By the test with H_2O_2 0.1–0.2 mg. of vanadium may be detected in a volume of 5 cc., provided the solution is strongly acid (2–6 n.) and a large excess of H_2O_2 is avoided. Molyb-

denum, even in large amount, would give with H_2O_2 a pure yellow color, not an orange or red one.

7. In the final test for vanadium with NH_4Cl 0.3–0.5 mg. can be detected if the solution is allowed to stand for several hours, after which small crystals of NH_4VO_3 can usually be seen adhering to the glass. Since this test is less delicate than the two preceding ones, it is useless to try it when these indicate that the vanadium present is less than 0.5 mg. It is, however, a very characteristic test, and is useful in estimating the amount of vanadium present.

Procedure 107.—*Detection of Tungsten when Phosphate is Present.*—In case phosphate was found present in P. 91, add to the filtrate from the HNO_3 precipitate (P. 106), at a volume of 50–60 cc., 15 n. NH_4OH, 1 cc. at a time, till the solution is alkaline; then add 20 cc. of 1 n. $Mg(NO_3)_2$ reagent, heat the mixture to boiling, and add gradually 5 cc. of 15 n. NH_4OH. Cool the mixture, and let it stand with occasional shaking for at least an hour. Filter off and reject the precipitate. Boil the filtrate till no more NH_3 comes off, add 3 cc. of 16 n. HNO_3, evaporate the mixture to 10 cc., and cool it completely; add 1 cc. of 16 n. HNO_3 and 5 cc. of water, and heat until crystalline salts have dissolved. (White or yellow precipitate, presence of TUNGSTEN.) Filter the mixture.

Reject the filtrate. Wash the precipitate, and treat it by P. 36, to confirm the presence of tungsten.

Notes.—1. Tungsten is precipitated completely with the tungsten and tantalum groups in P. 6, except when phosphate is present. In the latter case the tungsten passes into the $HClO_4$ solution, and is precipitated completely, together with the phosphate, by the iron in the acetate treatment (P. 92). After this precipitate is dissolved, the tungsten remains in solution with the phosphate up to this point.

2. In order to precipitate the tungsten as H_2WO_4, the phosphate must be completely removed. This is done by the addition of $Mg(NO_3)_2$; this reagent being first added in large excess to the hot solution, a large quantity of NH_4OH being then added, and the mixture being allowed to cool and stand.

3. With 2 mg. of tungsten alone a distinct precipitate of H_2WO_4 separates during the evaporation. But when vanadium is

present, the precipitate may not form till the mixture has been evaporated so that it solidifies on cooling, and has been reheated with HNO_3; in which case 2 mg. of tungsten are detected in the presence of 50 mg. of vanadium. Owing to the possibility of the precipitation of silica that has come from the vessels or reagents, the confirmatory test with $SnCl_2$ should always be applied.

ANALYSIS OF THE HYDROCARBONATE PRECIPITATE

Procedure 111.—*Separation of Aluminum from Zinc and Beryllium.*—Dissolve the $NaHCO_3$ precipitate (P. 101) by pouring a hot 5–15 cc. portion of 6 n. HCl repeatedly through the filter, using another portion of acid if the precipitate has not all dissolved. Add 1½ volumes of ether, and pass into the mixture in a small flask HCl gas until a single layer results and until fumes of HCl are copiously evolved, cooling the flask in running water. Cover the flask, and let the mixture stand for 15 minutes even if no precipitate has separated. (White crystalline precipitate, presence of ALUMINUM.) Filter it through an ordinary filter supported by a small hardened filter folded with it, or with the aid of suction through an asbestos filter (see Note 3); first moistening the filter with a mixture of two volumes of 12 n. HCl and three volumes of ether previously saturated with HCl gas. Wash the precipitate once with this mixture. During the filtration and washing keep the funnel covered with a watch-glass to prevent evaporation.

Treat the precipitate by P. 112. Treat the filtrate by P. 113.

Notes.—1. The precipitation of $AlCl_3 \cdot 6H_2O$ is complete only when the ether mixture is saturated with HCl gas, and when it is filtered before the gas escapes. The test is so delicate that 0.5 mg. of aluminum gives a precipitate in 15 cc. of the mixture within 15 minutes. It is also very characteristic; for no other element of the aluminum group is precipitated by this treatment, except chromium when present in moderate quantity, which cannot be the case here. A precipitate of NaCl, which separates here when the $NaHCO_3$ precipitate has not been thoroughly washed, might however be mistaken for the aluminum compound.

2. The ethereal solution of HCl, unlike the concentrated aqueous solution, does not disintegrate filter-paper rapidly, and the filtration can almost always be made with an ordinary filter supported by means of a hardened filter. This filtration is apt to be slow; and, when the precipitate is large, it is advantageous to filter through asbestos with the help of suction.

3. The asbestos filter may be made by pouring a dilute suspension of fine fibers of acid-washed asbestos through a perforated crucible till a mat 1 mm. thick is produced; or by placing in a funnel a compact conical wad of glass-wool not more than 10 mm. high with a flat upper surface, and pouring an asbestos suspension through it till a mat 1 mm. thick is produced.

4. A small precipitate at this point may arise from aluminum present as impurity in the NaOH or Na_2O_2 or from their action on porcelain (see Note 6, P. 95).

Procedure 112.—*Confirmation of Aluminum.*—Dissolve the HCl precipitate (P. 111), or a small portion of it if it is large, in 5 cc. of 2 n. HNO_3. To the solution add 5–10 cc. of water, 1–15 drops of 0.3 n. $Co(NO_3)_2$, and 3 cc. of 6 n. NH_4OH; and heat the mixture nearly to boiling. Filter with the aid of suction, and wash the precipitate with water, finally sucking it as dry as possible. Open the filter paper, tear off the portions to which no precipitate adheres, make a small roll of the remainder, wind a platinum wire around it in the form of a spiral helix, heat the paper in a flame till the carbon is burnt off, and ignite it for a minute or two at a bright-red heat. (Blue residue, presence of ALUMINUM.)

Notes.—1. A confirmatory test for aluminum is desirable mainly in order to distinguish $AlCl_3 \cdot 6H_2O$ from NaCl. The test with $Co(NO_3)_2$ depends upon the formation of a blue compound of the two oxides CoO and Al_2O_3, probably cobalt aluminate, $Co(AlO_2)_2$. It enables 0.5 mg. of aluminum to be detected, or even 0.2 mg. after a little practice. No other element gives a blue color to the ash. It is essential to have the aluminum present in excess; for otherwise the blue color is obscured by the black oxide of cobalt. Moreover, when sodium salts are present, the ash fuses together and the test is unsatisfactory. For these reasons the aluminum is precipitated with NH_4OH and the precipitate is washed. This ensures complete removal of the sodium salts, and serves in some measure to adjust the quantity of cobalt

associated with the aluminum to the size of the precipitate; for $Co(OH)_2$ is carried down by the $Al(OH)_3$ in greater quantity the larger the precipitate. Care should also be taken to add a number of drops of the $Co(NO_3)_2$ solution roughly proportional to the amount of the precipitate subjected to the test—using the lower limit, 1 drop, when it contains 1–5 mg. of aluminum, and the upper limit, 15 drops, when it contains 50–100 mg. of aluminum.

Procedure 113.—*Separation of Zinc from Beryllium.*—Evaporate the filtrate from the HCl precipitate (P. 111), first on a steam-bath till the ether is expelled, and then over a flame to 2–3 cc. Add 20 cc. of water and 6 n. NH_4OH till the solution after shaking smells of it, then 2–3 cc. more, and heat it nearly to boiling. (Precipitate, presence of BERYLLIUM or URANIUM.) Filter, and wash the precipitate.

Treat the filtrate by P. 114. Treat the precipitate by P. 115.

Notes.—1. The NH_4OH precipitate may contain, in addition to beryllium, the following elements: uranium, carried into the $NaHCO_3$ precipitate because of the presence of much aluminum, beryllium, or vanadium (Note 3, P. 101); titanium, not completely precipitated from the Na_2O_2 solution (Note 5, P. 95); aluminum, if in the HCl-ether treatment the solution was not saturated with HCl gas (Note 1, P. 111); iron, in extremely small quantity; and zinc, carried down with the beryllium. Of the zinc only a small proportion is precipitated, even when a large amount of beryllium is present; thus not more than 10% of 2 mg. or of 20 mg. of zinc is carried down with 50 mg. of beryllium.

Procedure 114.—*Detection of Zinc.*—To the ammoniacal filtrate (P. 113) in a small flask add 6 n. $HC_2H_3O_2$, 1 cc. at a time, till it is acid, heat it to 60–70°, insert a two-hole rubber stopper with an inlet tube, saturate the mixture with H_2S, close the flask, and let it stand for 5–10 minutes if no precipitate separates at once. (White flocculent precipitate, presence of ZINC.) Filter through a double filter (two filters folded together), and wash the precipitate once with a little water. Reject the filtrate.

Dissolve the precipitate, or a portion of it if it is large, by pouring a 5-cc. portion of 6 n. HNO_3 two or three times

through the filter. To the solution add from a dropper just one drop (0.03 cc.) of 0.3 n. $Co(NO_3)_2$ if the precipitate was small, or 2–3 drops if it was medium or large. Evaporate the mixture just to dryness, and add 1 cc. of 3 n. Na_2CO_3 solution if the precipitate was small, or 2–3 cc. if it was medium or large. Evaporate again to dryness, and ignite the residue at a low temperature by keeping the dish moving to and fro in a small flame till the purple color due to the cobalt disappears; let the casserole cool, and moisten the residue with water. (Green residue, presence of ZINC.) (If the ignited mass becomes black, owing to too strong heating, add a few drops of HNO_3, evaporate just to dryness, add the same quantity of 3 n. Na_2CO_3 as was added before, evaporate, and ignite carefully.)

Notes.—1. ZnS precipitates more rapidly, and in a somewhat more flocculent form, from a warm solution. Very small quantities of zinc (less than 1 mg.) may be missed unless a short time be allowed for the precipitate to coagulate. Contact with air is avoided so as to prevent the precipitation of sulfur; but a little may separate as a white turbidity on standing. A double filter is used, since ZnS is likely to pass through the filter.

2. The immediate formation of a white flocculent precipitate with H_2S in $HC_2H_3O_2$ solution is so characteristic as to be a sufficient test for zinc. The confirmatory test described in the last paragraph of the Procedure is useful when there is only a small non-coagulating precipitate which may be sulfur, or when the precipitate is dark colored owing to the presence of a small quantity of other elements.

3. The green compound obtained in the confirmatory test is a compound of cobalt and zinc oxides, perhaps cobalt zincate, $CoZnO_2$. Excess of cobalt must be avoided; for the black cobalt oxide completely obscures the green color. The repetition of the treatment suggested at the end of the Procedure is effective when the mass has been overheated, but not when too much cobalt has been added.

Procedure 115.—*Detection of Beryllium.*—Transfer the NH_4OH precipitate (P. 113) to a casserole, add 5–10 cc. of 6 n. $HC_2H_3O_2$, and evaporate the solution to about 0.5 cc.

Add 5–10 cc. of 99½% $HC_2H_3O_2$, and evaporate the mixture just to dryness, stirring it to prevent bumping. Add 10 cc. of dry $CHCl_3$, stir the residue with a pestle or heavy glass rod until it is crushed to small particles or dissolved, and filter the mixture through a dry filter.

Wash the solid residue with $CHCl_3$, and test it for uranium by P. 116.

Wash the chloroform solution in a separating funnel with 10 cc. of water, rejecting the wash-water. Evaporate the chloroform solution to complete dryness. Dissolve the residue by heating it with 3 cc. of 6 n. HNO_3, dilute with 10 cc. of water, add 6 n. NH_4OH until the solution after shaking smells of NH_3, then 1 cc. more, and heat the mixture nearly to boiling. (White flocculent precipitate, presence of BERYLLIUM.)

Notes.—1. By the evaporation with nearly anhydrous $HC_2H_3O_2$ there is formed a basic beryllium acetate, $BeO \cdot 3Be(C_2H_3O_2)_2$, which dissolves readily in $CHCl_3$, but not in water. By treating the residue with $CHCl_3$ and by washing the $CHCl_3$ solution with water the beryllium is freed from the other elements that may accompany it as impurities. Even when other elements are present in the residue, a large proportion of the beryllium is extracted by the $CHCl_3$, but some may also remain in the residue.

2. Of the other elements which may be present at this point (see Note 1, P. 113), only zinc dissolves in appreciable amount in the dry chloroform. If the chloroform were moist, however, some uranium (and perhaps other elements) would also dissolve. The washing with water removes from the chloroform solution any zinc, uranium, or other element that may have dissolved, while it extracts less than 3% of the beryllium. A precipitate now obtained with NH_4OH therefore shows the presence of beryllium. Even if the chloroform solution be washed with 1 n. HNO_3, instead of with water, and be allowed to stand with it, the loss of beryllium does not exceed 10%.

Procedure 116.—*Detection of Uranium.*—To the residue undissolved by $CHCl_3$ (P. 115) in a casserole add 20–50 cc. of freshly prepared 1% $NaHCO_3$ solution, heat the mixture to boiling, and filter it. Reject the residue. Acidify the filtrate with 6 n. HCl, adding 2–5 cc. in excess, boil it till the CO_2 is

expelled, and make it alkaline with 6 n. NH_4OH. (Yellow precipitate, presence of URANIUM.) Filter the mixture, and treat the precipitate by P. 105, to confirm uranium.

Notes.—1. The residue from the chloroform treatment may contain uranium, alone or with vanadium; also small amounts of aluminum, zinc, titanium, and iron (see Note 1, P. 113), and of beryllium. Of these elements uranium is the only one which might escape detection if not tested for here (see Note 3, P. 101).

2. The treatment with 1% $NaHCO_3$ solution dissolves the uranium and vanadium; but it leaves undissolved any beryllium in excess of 0.1 mg. and all the other elements named in the preceding Note. Hence the subsequent formation of a NH_4OH precipitate (of $(NH_4)_2U_2O_7$ or $UO_2NH_4VO_4$) enables any uranium which remained undissolved in the $NaHCO_3$ treatment of P. 101 to be detected.

3. Increasing the $NaHCO_3$ concentration would increase the quantity of beryllium dissolved (see Note 3, P. 101). Boiling the mixture has a similar effect. The volume used is adjusted to the size of the residue, since uranyl vanadate is only moderately soluble. In the unusual case that there is a large uranium residue, the concentration of the $NaHCO_3$ may also be increased, but not above 3%, since higher concentrations would dissolve titanium and iron. Some beryllium may then be dissolved; which would give a white precipitate with the NH_4OH, but would not precipitate with the ferrocyanide in the confirmatory test.

Tabular Outline XI

ANALYSIS OF THE NICKEL AND ZIRCONIUM GROUPS. ISOLATION OF THE RARE-EARTH GROUP

Peroxide precipitate (P. 97) from sulfide precipitate (P. 96): Mn, ‡Zn, Co, Ni, RE[a], as hydroxides (Mn as $MnO(OH)_2$; Co as $Co(OH)_3$). *Dissolve in HCl, evaporate, heat with HNO_3 and $KClO_3$ (P. 121).*

Peroxide precipitate (P. 95) from acetate precipitate (P. 92): In, Zr, Ti; RE, †Zn, Co, Ni; all as hydroxides.

Precipitate: MnO_2. *Add HNO_3 and H_2O_2 (P. 122).*

Filtrate: Nitrates of Zn, Co, Ni, RE. *Add NH_4OH, acidify slightly with $HC_2H_3O_2$, pass in H_2S (P. 123).*

Precipitate: ZnS, CoS, NiS. *Treat with cold 1 n. HCl (P. 124).*

Filtrate: RE. *Expel H_2S, add NH_4OH, filter, reject filtrate (P. 123).*

Precipitate: RE, as hydroxides. *Dissolve in HCl, evaporate, add a little dilute HF (P. 131).*

Solution: $Mn(NO_3)_2$. *Add BiO_2 (P. 122).*

Solution: $ZnCl_2$, †$CoCl_2$, †$NiCl_2$. *Add NaOH and Na_2O_2 (P. 124).*

Residue: CoS, NiS.

Filtrate: In, Zr, Ti; Zn, Co, Ni; all as fluorides. *Nearly neutralize with NH_4OH, add H_2S (P. 132).*

Precipitate: RE, ‡In, as fluorides. See T. XII.

Solution, purple: $HMnO_4$.

Filtrate: $NaHZnO_2$. *Add $(NH_4)_2S$ (P. 124).*

Precipitate: $Co(OH)_3$, $Ni(OH)_{2-3}$. *Add HCl and $KClO_3$ (P. 125)*

Precipitate: In$_2S_3$, ZnS, †CoS, †NiS. *Dissolve in HCl, boil, add NH_4OH (P. 133).*

Filtrate: H_2ZrF_6, H_2TiF_6, CoF_2, NiF_2. *Add H_2SO_4, evaporate, add water, H_2O_2, Na_2HPO_4 (P 134).*

Precipitate, white: ZnS. *Confirm zinc by P. 114.*

Solution: $CoCl_2$, $NiCl_2$. *Evaporate, add $HC_2H_3O_2$ and KNO_2 (P. 125).*

Precipitate: In$(OH)_3$. *Dissolve in $HC_2H_3O_2$, add H_2S (P. 133).*

Filtrate: Zn, Co, Ni. *Reject.*

Precipitate: $Zr(HPO_4)_2$.

Filtrate, orange: $TiO_2.H_2O_2$. *Add Na_2SO_3 (P. 135).*

Precipitate, yellow: $K_3Co(NO_2)_6$.

Filtrate: $NiCl_2$. *Add $(CH_3)_2C_2(NOH)_2$.*

Precipitate, red: Ni salt.

Precipitate, yellow: In_2S_3.

Precipitate: $Ti(HPO_4)_2$.

[a] RE denotes the elements of the rare-earth group.

† ‡ For the significance of these signs see page 9.

ANALYSIS OF THE NICKEL AND ZIRCONIUM GROUPS, AND ISOLATION OF THE RARE-EARTH GROUP

With Ellwood B. Spear and Howard I. Wood

Tabular Outline XI

See page 190.

General Discussion

D. 121. Union of the Material from the Two Peroxide Precipitates.—The peroxide precipitates from the two sources—the acetate treatment of P. 92 and the sulfide treatment of P. 96—are not immediately united for the reason (mentioned in D. 95) that the *zirconium group* (including indium, zirconium, and titanium) has by these treatments been largely separated from the *nickel group* (including manganese, zinc, cobalt, and nickel), and that this preliminary separation has important advantages that should not be sacrificed.

These advantages arise from the facts that, if all the elements were present together, (1) a large quantity of manganese, when later precipitated as the dioxide by nitric and chloric acids, would carry down all of a considerable quantity of titanium, and a large proportion, though not all, of the zirconium; and (2) that the subsequent separation of zinc, cobalt, and nickel from the other elements by passing hydrogen sulfide into a weakly acid acetate solution would not be practicable, since titanium does not remain dissolved under these conditions. Therefore, from the solution of the sodium peroxide precipitate obtained from the original sulfide precipitate, which contained most of the manganese, zinc, cobalt, and nickel, these four elements are first precipitated in the ways just indicated; and to the resulting filtrate, which may contain a large quantity of rare-earth elements, ammonium hydroxide is added, and the resulting precipitate is united with the peroxide precipitate coming from the acetate treatment, which contains all or nearly all of the indium, titanium, and zirconium, and may contain much or all of the rare-earth elements.

D. 122. Removal of the Nickel Group: Manganese, Zinc, Cobalt, Nickel (*P. 121, 123*).—The peroxide precipitate from the sulfide treatment is dissolved, and the manganese is first removed by the usual treatment with nitric and chloric acids. The precipitated manganese dioxide does not carry down appreciably the bivalent and trivalent elements which may be present with it in the solution. The next operations are the removal of the strong acid by evaporation, the production of a solution containing acetate and acetic acid in suitable proportions, and the saturation of this solution with hydrogen sulfide at 70–80°. Under these conditions zinc, cobalt, and nickel can be completely precipitated, and thereby separated from any rare-earth elements or other elements that may be present. (See also D. 97.) To secure in this way the complete precipitation of cobalt and nickel, the proportions of acetate and acetic acid must, to be sure, be carefully adjusted to those which the investigation showed to be suitable for the purpose; but with strict attention to the directions this is practicable. The sulfide precipitate is analyzed for the three common elements by the process given in A. A. Noyes' Qualitative Chemical Analysis, which process is based directly on the work of Noyes, Bray, and Spear.[1]

D. 123. Separation of the Zirconium Group (*Indium, Titanium, Zirconium*) *from the Rare-Earth Group* (*P. 131*).—Having separated, in the way just described, the elements of the nickel group from the rare-earth elements present in the original sulfide precipitate, it is natural to unite these latter elements with the peroxide precipitate from the original acetate treatment, since the elements of the rare-earth group may be present in either place.

It was desirable next to make use of some process by which the rare-earth group could be separated from the zirconium group, as well as from the small quantities of nickel-group elements that may be present. For this purpose two reagents, oxalic acid and hydrofluoric acid, were available; but the latter was adopted for the reasons stated below (see D. 127). Experiments showed that by using a small quantity of hydrofluoric acid (0.5–1.0 cc. of the 27 n. reagent) a fairly good separation could be secured. Thus

[1] Noyes, Bray, and Spear, *J. Am. Chem. Soc.*, 30, 481–563 (1908).

this dissolves over 100 mg. of indium, zirconium, and titanium, but only an inappreciable quantity of thorium or rare-earth elements. Indium, to be sure, when associated with much rare-earth element, may remain largely with the latter in the fluoride precipitate, making it necessary to provide for its detection in both groups. Scandium, moreover, is somewhat soluble in solutions containing fluoride-ion; and on this account only the minimum quantity of hydrofluoric acid is used and a small proportion of hydrochloric acid is added. Under these conditions, however, only a little scandium dissolves; thus only about ½ mg. for each cubic centimeter of the 27 n. hydrofluoric acid added, even when the scandium is present alone. On the whole, this plan of isolating the rare-earth group is probably as satisfactory as any that can be devised; and it was therefore adopted.

D. 124. Separation of Indium from Zirconium and Titanium and from Nickel-Group Elements (*P. 132, 133*).—A very simple method was found for separating the indium from the zirconium and titanium. Namely, merely by partially neutralizing with ammonium hydroxide the hydrofluoric acid solution resulting from the previous operation and saturating it with hydrogen sulfide the indium is completely precipitated, while the zirconium and titanium remain in solution. With the indium may precipitate, to be sure, at once any small quantity of zinc, and gradually a part of any moderate amount of cobalt or nickel, that may be present in the solution. The indium is, however, readily separated from these elements by dissolving the sulfides in acid and adding ammonium hydroxide, which precipitates only the indium. A very characteristic confirmatory test for this element was also discovered. This consists in dissolving the hydroxide in 6 normal acetic acid and saturating the solution with hydrogen sulfide. Under these conditions the indium separates as a bright-yellow precipitate.

D. 125. Separation and Detection of Zirconium and Titanium (*P. 134, 135*).—For the separation of zirconium from titanium there has here been adopted the process of Hillebrand,[1] which consists in adding sodium phosphate to a solution slightly acid

[1] Hillebrand, *Bull. U. S. Geol. Survey*, 176, 75 (1900); 700, 173 (1919).

with sulfuric acid and containing hydrogen peroxide. Thereby the zirconium is precipitated, while the titanium remains dissolved. The latter is shown to be present by the color of the solution; and from the filtrate it is precipitated as phosphate by destroying the hydrogen peroxide with sodium sulfite.

MODIFICATIONS OF THE PROCESS INVESTIGATED

D. 126. Methods of Separating Scandium from Titanium and Zirconium.—Before it was realized that the separation of the rare-earth elements from zirconium and titanium could be accomplished by the use of a very small volume of hydrofluoric acid solution, experiments were made on two other methods of separating from these two elements the scandium which would have dissolved in considerable quantity in a larger volume of that acid.

The first series of experiments showed that scandium, like titanium, is separated completely from zirconium when the latter is precipitated by sodium phosphate from a dilute sulfuric acid solution containing hydrogen peroxide (as is done in P. 134). They showed, however, that when the hydrogen peroxide in such a solution is destroyed by the addition of sulfite so as to precipitate the titanium as phosphate, this element may carry out with it nearly all the scandium even when as much as 5 mg. of it is present. This is true even though 30 mg. of scandium remain in solution when it is present alone.

The second series of experiments showed that scandium, like zirconium, can be completely precipitated, and thus separated from most of the titanium, by the method described by Classen [1] and by Walker,[2] which consists in dropping an acid solution of the three elements into a cold 3% hydrogen peroxide solution containing ammonium hydroxide. Some of the titanium, or even all of a small quantity, is carried down in the precipitate; but, by treating this precipitate by the first method just described, a satisfactory separation of the three elements can be effected. However, as this combination of the two methods seemed less simple than the fluoride separation, the latter was adopted.

[1] Classen, *Ber. deutsch. chem. Ges.*, **21**, 370 (1888).
[2] Walker, *J. Am. Chem. Soc.*, **20**, 513 (1898).

D. 127. Comparative Advantages of Oxalic Acid and Hydrofluoric Acid for the Isolation of the Rare-Earth Group (P. 131).—For the separation of the rare-earth group from the other elements oxalic acid is commonly employed in quantitative determinations, instead of hydrofluoric acid. Therefore two series of experiments were made with the various elements to determine which of these two reagents effected the more complete separation. 500 mg. of each of the common elements, 100 mg. of each of four typical elements of the rare-earth group (thorium, scandium, cerium, yttrium), and 100 mg. of most of the other rarer elements of the aluminum and nickel groups, in the form of the dry chloride or nitrate, were therefore treated with 25 cc. of a 48% solution of hydrofluoric acid in one series of experiments, and with 50 cc. of nearly saturated oxalic acid solution in another series of experiments, first in the cold and then at a nearly boiling temperature. The results of these experiments showed that both reagents precipitate all the rare-earth elements, except scandium, nearly completely; but that the precipitation of the fluorides is a little more complete. In the case of scandium, experiments made in the way just described showed that about 15 mg. of this element dissolve in the hydrofluoric acid, and about 25 mg. of it in the oxalic acid, but that any quantity present in excess of these amounts remains with the rare-earths in the fluoride or oxalate precipitate. While the preceding experiments showed no very marked differences in the behavior of the rare-earths towards the two reagents, this was found not to be the case with the other elements. Thus, in every case these elements were dissolved completely by the large excess of hydrofluoric acid; but several of them, when present in large quantity, notably the bivalent elements zinc, manganese, nickel, and cobalt, remained largely undissolved when oxalic acid was employed. These facts made it evident that hydrofluoric acid is a more generally applicable reagent for the separation of the rare-earths, and that it is advisable to employ it when bivalent elements may be present, in spite of the somewhat greater manipulative convenience of using oxalic acid.

D. 128. Best Stage in the Analysis for Isolating the Rare-Earth Group (P. 131).—While the above described experiments proved that the rare-earth group, except scandium, could be sepa-

rated fairly well at an early stage in the analysis from all the elements of the aluminum and nickel groups by means of hydrofluoric acid, yet they showed that a large quantity of concentrated hydrofluoric acid must be employed for the purpose. This has the disadvantages that the use of so much of this reagent is inconvenient, and that scandium when present in considerable amount divides itself between the precipitate and solution.

These considerations made it seem advisable to postpone the isolation of the rare-earth group with hydrofluoric acid to a late stage in the analysis, first removing such of the other elements as can be readily separated by other reagents. In the scheme that is adopted the hydrofluoric acid treatment is therefore introduced (in P. 131) only after the iron and gallium and the aluminum group have been removed and the nickel-group elements have been largely eliminated.

It was almost certain that the rare-earth elements would behave throughout this process like zirconium and titanium, and would be left with them at the end. To make sure that this was the case, experiments were tried. These showed that the rare-earths are not removed from a hydrochloric acid solution by ether, and that they are completely precipitated by sodium hydroxide and peroxide.

ANALYSIS OF THE NICKEL AND ZIRCONIUM GROUPS, AND ISOLATION OF THE RARE-EARTH GROUP

Tabular Outline XI

See page 190.

Procedures and Notes

NICKEL GROUP

Procedure 121.—*Separation of Manganese from Cobalt, Nickel, Zinc, and Rare-Earth Elements.*—Transfer to a casserole the Na_2O_2 precipitate (P. 97) obtained from the solution of the $(NH_4)_2S$ precipitate; add 5–20 cc. of 6 n. HCl, and boil the mixture gently till the precipitate is dissolved. Filter (to remove the paper), and evaporate the filtrate almost to dryness. Add 2–3 cc. of 16 n. HNO_3 and evaporate to about 1 cc. Rinse the residue into a 50-cc. wide-mouth conical flask with 10 cc. of 16 n. HNO_3. Place the flask in a beaker of boiling water, add gradually 0.5 cc. of powdered $KClO_3$, and continue to heat the mixture for 1–2 minutes. (Black precipitate, presence of MANGANESE.)

In case there is no precipitate, treat the solution by P. 123.

In case there is a precipitate, add gradually powdered $KClO_3$, 0.5 cc. at a time, heating (in the water-bath) for 1–2 minutes after each addition, till no further precipitation takes place, not adding more than 3 cc. in any case. Filter the mixture with the aid of suction through an asbestos filter (prepared as described in Note 3, P. 111). Collect the filtrate in a test-tube placed within the filter-flask. Wash the precipitate with a little water, and treat it by P. 122. Treat the filtrate by P. 123.

Notes.—1. The precipitate is heated with HCl, rather than with HNO_3, so as to dissolve $MnO(OH)_2$. The solution is then evaporated with HNO_3 to destroy the HCl.

2. By $HClO_3$ in hot HNO_3 solution (but not by HNO_3 alone) manganous salts are rapidly oxidized with precipitation of MnO_2 and formation of ClO_2 gas. If any reducing agent is present, it

has to be destroyed by the $HClO_3$ before the precipitate will form. The presence of filter paper is especially to be avoided, since it is only slowly destroyed and may prevent the precipitation of even a considerable quantity of manganese. For the same reason, if a fresh portion of HNO_3 is added to the mixture, the NO_2 should be previously removed from the acid by heating it with $KClO_3$.

3. The $KClO_3$ is added gradually so as to avoid too violent action in case much manganese is present and to prevent the use of an unnecessary excess in any case. The mixture is heated in a water-bath, instead of directly over a flame, in order to avoid the risk of the acid being thrown out of the flask by bumping, and in order to obviate the danger of an explosion, which might occur if a large quantity of ClO_2 vapor were suddenly produced and exposed to a temperature above 100°. In this Procedure, where the mixture is heated in a water-bath, there is no danger of explosion provided the $KClO_3$ is added a little at a time.

4. This method of separating manganese is satisfactory, provided only the elements precipitated with it by $(NH_4)_2S$ are present. If, however, titanium, zirconium, or vanadium (previously removed in the acetate treatment in P. 92) were in the solution, a large proportion of any of these elements might be carried out by the manganese, and the element might escape detection; thus 50 mg. of titanium may be carried down completely by 500 mg. of manganese, 10 mg. of vanadium nearly completely by 250 mg., and 30 mg. out of 50 mg. of zirconium by 500 mg.

Procedure 122.—*Confirmation of Manganese.*—Pour twice through the filter containing the $HClO_3$ precipitate (P. 121) a warm 5-cc. portion of 6 n. HNO_3 to which 10 drops of 1 f. H_2O_2 solution have been added. Collect the filtrate in a test-tube, cool it, add to it solid BiO_2, 0.1 cc. at a time, till a purple color results, or till some of the brown solid remains undissolved; and let the solid settle. (Purple solution, presence of MANGANESE.)

Notes.—1. This confirmatory test for manganese is usually superfluous, since the precipitation of manganese by $HClO_3$ is highly characteristic. A small amount of H_2O_2 is used so as to dissolve only a part of a large precipitate. An excess of BiO_2 must be added, since otherwise the manganese may be oxidized only to MnO_2. Commercial bismuth dioxide, also often called sodium bismuthate, is a mixture of bismuth compounds which prob-

ably owes its oxidizing power to the presence of the dioxide BiO_2. When it is not available, PbO_2 may be substituted for it; but in that case the mixture must be boiled with 0.5 cc. of solid PbO_2 for 2 or 3 minutes.

Procedure 123.—*Separation of Cobalt, Nickel, and Zinc from Rare-Earth Elements.*—Evaporate the filtrate from the $HClO_3$ precipitate (P. 121) to 1–2 cc. Add 30 cc. of cold water, and 6 n. NH_4OH to slight alkaline reaction, then just 2 cc. more. (No precipitate, absence of RARE-EARTH ELEMENTS.)

In case NH_4OH produces no precipitate, pass into the mixture a slow current of H_2S till after shaking its odor is perceptible; adding more 6 n. NH_4OH if the solution does not remain alkaline. Heat the mixture nearly to boiling. (Black precipitate, presence of COBALT or NICKEL; white precipitate, presence of ZINC.) Filter, and wash the precipitate. Reject the filtrate; treat the precipitate at once by P. 124.

In case NH_4OH produces a precipitate, add at once just 3 cc. of 6 n. $HC_2H_3O_2$, or more if the solution does not redden litmus paper. (If a precipitate remains, filter it out, and unite it with the NH_4OH precipitate later obtained as described in the final paragraph.) To the clear solution add 10 cc. of 3 n. $NH_4C_2H_3O_2$. Heat the mixture to 70–80°, and pass through it a slow current of H_2S till, after letting the mixture stand for 5 minutes, and shaking, it smells strongly of H_2S. Cool the mixture, saturate it with H_2S, heat it to 70–80°, and again saturate it with H_2S. (Black precipitate, presence of COBALT or NICKEL; white precipitate, presence of ZINC.) Filter the hot mixture, and wash the precipitate with cold H_2S water.

Treat the precipitate at once by P. 124.

Treat the filtrate as follows. Boil it till the H_2S is expelled, filter off and reject any small precipitate, and add 6 n. NH_4OH till the solution smells of it and then 2 cc. more. (White precipitate, presence of RARE-EARTH ELEMENTS.) Filter out, and wash the precipitate. Reject the filtrate. Treat the precipitate by P. 131, uniting it with the Na_2O_2 precipitate from P. 95.

Notes.—1. The HNO_3 solution is made alkaline with NH_4OH in order to determine whether rare-earth elements are absent; for when they are absent the cobalt, nickel, and zinc sulfides may be precipitated in alkaline solution. This has the advantage that these elements are then thrown down at once, while from an $HC_2H_3O_2$ solution the nickel and cobalt are only slowly precipitated. As to their precipitation by H_2S from alkaline solution see Notes 1–4, P. 96.

2. In order to secure complete precipitation of cobalt and nickel by H_2S in acid solution, the ratio of $HC_2H_3O_2$ to $NH_4C_2H_3O_2$ must not be much greater than 1 : 1. By following the Procedure there will be introduced at the start 6 milliequivalents of $HC_2H_3O_2$ and 36 of $NH_4C_2H_3O_2$, the excess of the latter acting as a buffer against the liberation of acid during the precipitation of the sulfides. Zinc is completely precipitated from $HC_2H_3O_2$ solution when only little more acetate is present than is required to combine with any stronger acid set free by the precipitation.

3. H_2S is first passed slowly into the hot solution so as to cause the precipitates, especially the ZnS, to separate in a form in which they can be more readily filtered and washed. The heating also serves to hasten the precipitation of nickel and cobalt, which even in hot solution is complete only after a few minutes. The solution is finally cooled, resaturated with H_2S, and reheated in order to ensure the precipitation of 1 mg. of nickel or cobalt.

4. In case NH_4OH produces a precipitate which does not redissolve on acidifying with $HC_2H_3O_2$, this may consist of zirconium or thorium; for the hydroxide of zirconium dissolves scarcely at all, and that of thorium not completely, in $HC_2H_3O_2$ in the presence of acetate. The hydroxides of the trivalent elements of the rare-earth group, on the other hand, dissolve readily.

Procedure 124.—*Separation of Zinc from Cobalt and Nickel.*—In case the H_2S precipitate (P. 123) was white, treat it by the second paragraph of P. 114 to test for zinc.

In case the H_2S precipitate (P. 123) was at all darkened, transfer it to a casserole; add 10–30 cc. of 1 n. HCl, stir the (cold) mixture frequently for 5 minutes, and filter it. (Black residue, presence of COBALT or NICKEL.) Wash the residue, and treat it by P. 125 (after uniting it with the Na_2O_2 precipitate obtained from the filtrate). Boil the filtrate till the H_2S is completely expelled, make the mixture alkaline with 6 n.

NaOH, cool it, and add gradually 0.5–1.0 cc. of Na_2O_2 powder. Boil the mixture gently for 2–3 minutes, cool it, and filter it. (Black precipitate, presence of COBALT; green precipitate, presence of NICKEL.)

Wash the precipitate, unite it with the residue undissolved by the 1 n. HCl, and treat the mixture by P. 125.

To the filtrate add 3–10 drops of 6 n. $(NH_4)_2S$ solution. (White precipitate, presence of ZINC.) To confirm the presence of zinc, filter out and wash the precipitate, and treat it by the second paragraph of P. 114.

Notes.—1. The treatment with 1 n. HCl serves to extract from the CoS and NiS nearly all the zinc which may be present in this precipitate because of its having been carried down in the Na_2O_2 precipitate, as described in Note 4, P. 97. A small proportion of the cobalt and nickel present (5–20%) always dissolves in the 1 n. HCl, and the subsequent treatment with Na_2O_2 serves to separate these elements from the zinc. This Na_2O_2 separation is satisfactory when, as in this HCl solution, the cobalt and nickel are present in small quantity; for then only an insignificant amount of zinc is carried down with them.

2. This Procedure must always be followed in order to determine whether or not zinc is present in the substance, unless a satisfactory test for it has already been obtained in P. 114, or unless the original Na_2O_2 precipitate (P. 97) was small. In either of these two cases this Procedure may be omitted and the H_2S precipitate (P. 123) treated directly by P. 125.

3. The fact that CoS and NiS do not dissolve readily in 1 n. HCl seems inconsistent with the non-precipitation of cobalt and nickel by H_2S with the tellurium and copper groups from a solution which is 0.3 normal in acid. This behavior probably arises from the fact that these sulfides exist in at least two allotropic forms of different solubilities. The form that is first produced when sulfide-ion is brought together with nickel-ion or cobalt-ion is soluble in dilute acid; but this form changes on standing or heating into a less soluble form (or forms). The partial solution in dilute HCl of the precipitated CoS or NiS may be attributed mainly to the presence of the more soluble form. Its proportion will be smaller the longer the precipitate has been heated, the longer it has been allowed to stand, and the higher the concentration of hydrogen-ion in the solution at the time of precipitation.

The less soluble forms of the sulfides do not dissolve in the 1 n. HCl to an extent corresponding to their solubilities; for their rate of solution is extremely small. Their rate of precipitation is also small, even when the hydrogen-ion is only 10^{-5} normal (see Note 1, P. 123).

4. The NaOH precipitates cobalt as blue $CoCl(OH)$, changing to pink $Co(OH)_2$; and it precipitates nickel as light-green $Ni(OH)_2$. By the addition of Na_2O_2 the cobalt is oxidized to black $Co(OH)_3$ and its precipitation made more complete. The nickel precipitate retains its green color, though some of it may be oxidized to $Ni(OH)_3$, since the black color of this substance is often observed when the precipitate is treated with acid in P. 125.

5. Only a small quantity (0.5–1.0 cc.) of Na_2O_2 powder is added, since the quantity of cobalt and nickel dissolved by the dilute HCl never exceeds 100 mg. The solution is subsequently boiled to decompose the excess of Na_2O_2, since otherwise it would destroy the $(NH_4)_2S$ added to precipitate the zinc.

Procedure 125.—*Detection of Cobalt and Nickel.*—Transfer the Na_2O_2 precipitate and the residue from the HCl treatment (P. 124) to a casserole, add 5–15 cc. of HCl, heat the mixture nearly to boiling, and sprinkle into it 0.1–0.3 cc. of powdered $KClO_3$. Filter out any residue of sulfur, and evaporate the solution just to dryness. Dissolve the residue in 5 cc. of 6 n. $HC_2H_3O_2$. To the solution in a test-tube add 3 cc. of 6 n. KNO_2 solution, and let it stand with occasional shaking for at least 15 minutes. (Yellow precipitate, presence of COBALT.) If a considerable precipitate forms, add to the mixture 10 cc. more of 6 n. KNO_2 solution and 4 cc. of powdered KCl, and let it stand with frequent shaking for at least 15 minutes. Filter. Reject the precipitate.

To one fourth of the filtrate add 10 cc. of water and 4 cc. of 0.1 n. diacetyldioxime solution in ethyl alcohol, heat the mixture nearly to boiling, and let it stand 5–10 minutes. (Red precipitate, presence of NICKEL.)

Reject the remainder of the filtrate.

Notes.—1. Only a small quantity (3 cc.) of KNO_2 solution is added at first, since in the small volume of solution this suffices to give a distinct precipitate with less than 1 mg. of cobalt within 15 minutes, and since with this small quantity there is no danger that

nickel will be precipitated. In case a considerable precipitate forms, a much larger quantity of the KNO_2 reagent is added, together with enough solid KCl to nearly saturate the solution, in order to precipitate nearly all of the cobalt; for the presence of much cobalt interferes with the subsequent test for nickel. Even though under these conditions some nickel may be precipitated, especially when much of it is present together with a large quantity of cobalt, only a small fraction of the nickel is ever carried down.

2. This separation of cobalt from nickel depends on the oxidation of the cobalt from the bivalent to the trivalent state by HNO_2, the conversion of the cobaltic ion, Co^{+++}, into the very stable complex anion $Co(NO_2)_6^{---}$, and the precipitation of the latter in the form of the slightly soluble $K_3Co(NO_2)_6$ (potassium cobaltinitrite). It is evident that a large concentration of HNO_2 tends to hasten the oxidation, that a large concentration of NO_2^- causes more complete conversion of Co^{+++} into $Co(NO_2)_6^{---}$, and that a large concentration of K^+ must diminish the solubility of the $K_3Co(NO_2)_6$. These conditions are provided for in the Procedure. The nickel is not appreciably oxidized by HNO_2 to the nickelic state. In case it is precipitated by KNO_2, it separates in the form of the (fairly soluble) potassium nickelous nitrite, $K_4Ni(NO_2)_6$.

3. Only one fourth of the filtrate is used for the nickel test with diacetyldioxime, since this suffices to give the desired delicacy, since it enables the quantity of nickel present to be better estimated, and since it diminishes the quantity of cobalt present in the solution tested. It is desirable that not much cobalt be present, since a smaller volume of the (rather expensive) reagent is then required; for a quantity of the diacetyldioxime equivalent to the cobalt present must be added before a small quantity of nickel will yield a precipitate. This is probably due to the fact that the cobalt combines with the reagent forming a soluble complex salt.

4. Diacetyldioxime is a weak monobasic organic acid of the composition $(CH_3)_2C_2(NOH)_2$. The brilliant red substance is its nickel salt, formed by replacing by one nickel atom one hydrogen atom in each of two diacetyldioxime molecules. The precipitate is so slightly soluble, so voluminous, and so highly colored that less than 0.1 mg. of nickel can be detected in the solution tested.

ISOLATION OF THE RARE-EARTH GROUP

Procedure 131.—*Separation of the Rare-Earth Group from Indium, Zirconium, and Titanium.*—Transfer the Na_2O_2 precipitate (P. 95) and the NH_4OH precipitate (P. 123) to a casserole, add 5–10 cc. of 6 n. HCl, remove the filter-paper with a glass rod, and (without filtering) evaporate the mixture almost to dryness. Transfer the mixture to a platinum dish, rinsing it in with water, and evaporate it to complete dryness on a steam-bath. To the residue add 2 cc. of water, just 0.5 cc. of 27 n. HF, just 1.0 cc. of 6 n. HCl, and 9 cc. of water. If there is a large residue, add 0.1–0.5 cc. more HF, a few drops at a time, as long as the residue is dissolving. Heat the mixture on a steam-bath for 5 minutes. (Precipitate, presence of RARE-EARTH GROUP.) Filter through a paper supported in a bakelite or hard-rubber funnel, collecting the filtrate in a platinum dish or crucible. Wash the precipitate.

Treat the filtrate by P. 132. Treat the precipitate by P. 141.

Notes.—1. The Na_2O_2 precipitate (P. 95) may contain, in addition to the elements normally present whose detection is provided for (indium, zirconium, titanium, and rare-earth elements), various other elements which need not be tested for. Of these, only nickel and cobalt are likely to be present in considerable quantity (up to 20 mg.). The NH_4OH precipitate (P. 123) usually contains only rare-earth elements.

2. The precipitates are treated first with HCl (rather than directly with HF) so as to dissolve the higher oxides of nickel, cobalt, and manganese that may be present in the Na_2O_2 precipitate. The solution is evaporated almost to dryness before transferring it to a platinum dish, since otherwise considerable platinum is dissolved, especially when nickel is present. The mixture is not filtered, so as not to remove prior to the HF treatment any undissolved substances, which might contain titanium, zirconium, or thorium (see Note 1, P. 93).

3. By the addition of only 0.5 cc. of 27 n. HF, 1.0 cc. of 6 n. HCl, and 9 cc. of water all of the rare-earth elements are so completely precipitated that less than ½ mg. of any one of them remains in solution. It is not ordinarily necessary to add more than 0.5 cc. of HF solution in order to dissolve completely the

zirconium, titanium, and indium, since 100 mg. of any of these elements dissolve readily in this volume. Only in case as much as 300–500 mg. of these elements were present would it be necessary to add 1.0–2.0 cc. of the HF solution. If a much larger volume of the 27 n. HF were added, a considerable quantity of scandium would dissolve; namely, about ½ mg. of it per cubic centimeter of 27 n. HF added.

4. The HCl is added in order to depress the ionization of the HF, and thus diminish the solubility of ScF_3; for this solubility increases with the concentration of fluoride-ion owing to formation of complex ions, such as ScF_4^-. A small quantity of HCl suffices for this purpose; thus, when 1 cc. is used, 1 mg. of scandium is largely precipitated, but this quantity yields no precipitate when no HCl is added. A much larger quantity should not be added, since high hydrogen-ion concentration increases the solubilities of scandium and rare-earth fluorides, owing to the displacement of the HF; thus 1 mg. of scandium gives no precipitate if 5 cc. of 6 n. HCl are added.

5. When only 1 mg. of titanium or zirconium is present, it is extracted from 100 mg. of rare-earth elements, but nearly all of a small quantity of indium may be retained in the precipitate when a large quantity of rare-earths is present (thus 4 mg. out of 5 mg. of indium when 100 mg. of cerium are present). Indium must therefore be tested for both in the solution and precipitate. The small quantities of zinc, cobalt, and nickel that may be present here dissolve in the HF when they are present alone; but whether they are completely extracted from a rare-earth precipitate has not been determined.

6. If alkaline-earth elements were present in the solution, calcium or magnesium would be precipitated by HF completely, and barium or strontium would be precipitated partially, together with the rare-earth fluorides. These alkaline-earth elements, however, have been previously eliminated by the acetate and sulfide precipitations (P. 92 and 96).

ZIRCONIUM GROUP

Procedure 132.—*Separation of Indium from Zirconium and Titanium.*—Neutralize the filtrate * from the HF precipitate (P. 131) with 6 n. NH_4OH, adding it towards the end a few drops at a time till the mixture becomes alkaline to litmus paper; then add 27 n. HF, only one drop (0.03 cc.) at a time, till it becomes acid, and finally one drop more; saturate it with H_2S, and let it stand 5–10 minutes. (Yellowish-white precipitate, presence of INDIUM; white precipitate, presence of ZINC.) Filter the mixture through a small filter supported in a bakelite or hard-rubber funnel, and wash the precipitate. (If there is much precipitate, boil the filtrate till the H_2S is expelled, and treat it again by the whole of this Procedure. Unite any precipitate with the previous one.)

Treat the precipitate by P. 133, and the filtrate by P. 134.

Notes.—1. In this separation 1 mg. of indium gives a precipitate in the presence of 100 mg. of zirconium and titanium, and 100 mg. of the last two elements remain in solution. The precipitation of indium is complete, however, only if an excess of free HF is avoided; thus, if 7 drops, instead of 2 drops, of 27 n. HF are added to the neutralized solution, 2 mg. of indium will not precipitate. Since, when much indium is present, enough free HF is formed by the metathesis to prevent complete precipitation, it is directed in this case to neutralize the filtrate, add a little HF, and repeat the treatment with H_2S.

2. A few milligrams of zinc and a larger quantity of nickel and cobalt may be present in this solution, because they were carried down in the acetate precipitate (in P. 92) and were not dissolved in the Na_2O_2 treatment (in P. 95). Any zinc so present is, like the indium, precipitated by the H_2S in this procedure. Of the nickel and cobalt present only a small proportion (thus 1–2 mg. out of 30–50 mg.) is precipitated within ten minutes, but a larger quantity comes down on longer standing or when indium is also present.

3. Indium, when present alone in small amount, yields a turbid suspension with a yellowish tint; when in large amount it gives a

* For practice-analyses use a solution made by evaporating a mixture of test-solutions of indium, titanium, and zirconium to dryness on a steam-bath, and adding to the residue 0.5 cc. of 27 n. HF, 1 cc. of 6 n. HCl, and 10 cc. of water.

slowly settling light-yellow precipitate. The precipitate may, however, be darkened by the presence of nickel or cobalt. Owing to the possible presence of these elements and of zinc, the confirmatory test for indium (in P. 133) should always be tried, whatever the color of the precipitate.

Procedure 133.—*Confirmation of Indium.*—Dissolve the H_2S precipitate (P. 132) by pouring a hot 5-cc. portion of 6 n. HCl repeatedly through the filter, adding a few drops of 6 n. HNO_3 if there is a black residue. Boil the solution till the H_2S is expelled, and filter out any residue. To the solution add 6 n. NH_4OH till it is alkaline, then 1 cc. more. (White precipitate, presence of INDIUM.) Filter through a small filter, and wash the precipitate.

Reject the filtrate; or test it for zinc, nickel, or cobalt, by making it slightly acid with $HC_2H_3O_2$, saturating it with H_2S, heating it to 70–80°, and letting it stand for 5 minutes.

Pour repeatedly through the filter containing the NH_4OH precipitate a hot 10-cc. portion of 6 n. $HC_2H_3O_2$, saturate the solution with H_2S, and let it stand for 10 minutes. (Yellow flocculent precipitate, presence of INDIUM.)

Notes.—1. Even ½ mg. of indium is precipitated from the 10 cc. of 6 n. $HC_2H_3O_2$ solution by H_2S within 10 minutes. The precipitate, even with this quantity of indium, has a deep-yellow color and coagulates and settles rapidly; thus differing markedly from the precipitate produced in the NH_4F solution in P. 132.

2. Zinc, if even ½ mg. were present in the 6 n. $HC_2H_3O_2$, would give a precipitate with the H_2S; but the precipitate would be white, not yellow. Moreover, zinc cannot still be present, since it would not have been precipitated by the NH_4OH previously added to the HCl solution. Nickel and cobalt are also not precipitated by the NH_4OH, but even if a small quantity were present in the $HC_2H_3O_2$ solution, it would not precipitate with H_2S. Iron, if present, would give with H_2S a white precipitate of sulfur; but little, if any, iron can be here, since it does not precipitate with H_2S in the NH_4F solution (in P. 132).

Procedure 134.—*Detection of Zirconium and Titanium.*—To the HF solution (P. 132) in a platinum dish add 3 cc. of 6 n. H_2SO_4, and evaporate the solution until the H_2SO_4 fumes.

Cool the solution, add to it 5 cc. of water and 10 cc. of 1 f. H_2O_2, and filter out any residue. (Orange-yellow or orange-red solution, presence of TITANIUM.) Add to the solution 10 cc. of 1 n. Na_2HPO_4, and let it stand for half an hour. (White precipitate, presence of ZIRCONIUM.) Filter.

Treat the precipitate no further. Add to the filtrate powdered Na_2SO_3, a little at a time, till it is decolorized, and let it stand at least half an hour. (White precipitate, presence of TITANIUM.)

Notes.—1. As to the test for titanium with H_2O_2, and the precipitation of zirconium and titanium as phosphates, see Notes 1–3, P. 43.

2. Zirconium in the material analyzed is normally found at this point; but it must also be tested for in the tantalum group in P. 49, especially when phosphate is also present (see Note 6, P. 6). On the other hand, the amount of titanium found here will usually not exceed 4 mg., unless much zirconium is present (see Notes 4 and 5, P. 6).

3. Besides titanium and zirconium, the solution from P. 132 may contain nickel and cobalt (see Note 2, P. 132), scandium if the directions in P. 131 were not followed (see Notes 3 and 4, P. 131), indium if the HF concentration in P. 132 were too high (see Note 1, P. 132), and uranium (see Note 3, P. 97); but none of them in sufficient amount to interfere with the zirconium and titanium tests. If scandium is present at this point alone or with zirconium, it is not precipitated by phosphate in dilute acid solution, but it is carried down by titanium when its phosphate is precipitated by the addition of Na_2SO_3. While indium alone is not precipitated by phosphate in the dilute acid solution, it would be carried down always to a considerable extent, and sometimes completely, with the zirconium or with the titanium. Thorium if present would precipitate as phosphate (with zirconium); but it should have been completely removed as fluoride in P. 131.

4. The recently discovered element hafnium has not been included in the investigations upon this System of Analysis; but, since its properties are known to be very similar to those of zirconium, it would presumably be found with it in the first phosphate precipitate obtained in this Procedure. The only question would seem to be how much of it would dissolve in the small quantity of 27 n. HF used in P. 131.

ANALYSIS OF THE RARE-EARTH GROUP

With Isaburo Wada

Tabular Outline XII

See page 210.

General Discussion

Acknowledgment.—Almost all the experimental work upon the fluoride and iodate separations (D. 141–144), and also that on the fractionation-processes and on the nitrate fusion outlined in D. 145–149, was done, in association with one of the authors (A. A. Noyes), by Isaburo Wada, now director of the Wada Research Laboratory of the Institute of Physical and Chemical Research at Tokyo. An extended preliminary study of rare-earth separations had previously been made by William C. Arsem.

D. 141. Extraction of Scandium from the Rare-Earth Fluorides (P. 141).—The fact that scandium fluoride is known to be somewhat soluble in excess of hydrofluoric acid suggested that scandium might be separated from the other rare-earth elements by extracting it from the fluoride precipitate with acid ammonium fluoride. It was found, in fact, that even 100 mg. of scandium as precipitated fluoride are dissolved by 25 cc. of a solution of acid ammonium fluoride. Experiments were then made with the elements thorium, cerium, and yttrium, which showed that their fluorides are all practically insoluble in acid ammonium fluoride solution. As it was further found that even 1 mg. of scandium is extracted by acid ammonium fluoride solution from a fluoride precipitate containing even 100 mg. of thorium, cerium, or yttrium, the plan was adopted of separating scandium from the other rare-earth elements by treating the original hydrofluoric acid precipitate (of P. 131) with a mixture of two volumes of 6 normal NH_4OH and one volume of 27 normal HF solution.

Similar experiments were made on the solubilities of the rare-earth oxalates in acid ammonium oxalate. These showed that at least 10 mg. of scandium as precipitated oxalate are dissolved by 30 cc. of a solution of acid ammonium oxalate; but that the oxalate of thorium is readily soluble in this solution (as was previ-

Tabular Outline XII

Analysis of the rare-earth group

Precipitate of fluorides of Sc, ‡In, RE[a] (P. 131). *Extract with acid NH_4F (P. 141).*

Solution: NH_4ScF_4. *Fume with H_2SO_4 (P. 142).*

Precipitate: $Sc_2(SO_4)_3$. *Add water and NH_4OH, filter.*

Precipitate: $Sc(OH)_3$. *Dissolve in HCl, evaporate, add one drop of 27 n. HF.*

Precipitate: ScF_3. *Add acid NH_4F.*

Solution: NH_4ScF_4.

Residue: RE, In, as fluorides. *Fume with H_2SO_4, add water and NH_4OH, filter out the precipitate, dissolve it in $HC_2H_3O_2$, pass in H_2S (P. 143).*

Precipitate, yellow: In_2S_3.

Filtrate: RE as acetates. *Evaporate, add HNO_3, $KClO_3$, and KIO_3 (P. 143).*

Precipitate: $Th(IO_3)_4$, $Ce(IO_3)_4$. *Add H_2O_2, HNO_3, and KIO_3 (P. 144).*

Residue: $Th(IO_3)_4$. *Evaporate with HCl, add H_2O_2 (P. 145).*

Precipitate, white: $ThO_2.H_2O_2$.

Solution: $Ce(IO_3)_3$. *Add NH_4OH (P. 146).*

Precipitate, orange: $CeO_2.H_2O_2$.

Filtrate: other RE. *Add NH_4OH, filter, dissolve the precipitate in HCl, add K_2CO_3 (P. 147).*

Precipitate: LANTHANUM SUBGROUP: La, Pr, *Nd, *Sm, *Eu; ‡Yttrium subgroup; all as $K\overline{RE}(CO_3)_2$.

Filtrate: YTTRIUM SUBGROUP: Gd, Tb, Dy, Ho, Er, Tu, Yb, Lu, Y, as $K\overline{RE}(CO_3)_2$. Also †Nd, †Sm, †Eu. *Add HCl, then NH_4OH, filter. Dissolve the precipitate in HCl, evaporate, add $HCHO_2$ and NH_4CHO_2 (P. 148).*

Precipitate: Nd, Sm, Eu. ‡Yttrium subgroup. *Fuse with $NaNO_3$, extract with water, then with $HC_2H_3O_2$ and $NaC_2H_3O_2$ (P. 149).*

Filtrate: Yttrium subgroup.

Residue, brown: PrO_2, †La_2O_3, ‡Nd_2O_3.

Water extract: *La, †Nd, †Sm. *Add NH_4OH, filter, heat precipitate with K_2CO_3.*

Precipitate: $KLa(CO_3)_2$.

Filtrate: Nd, Sm.

Acetate extract: *Nd, *Sm, †La, ‡Pr. Yttrium subgroup.

[a] The symbol RE denotes the elements of the rare-earth group.

* † ‡ For the significance of these signs see page 9.

ously known), and that that of yttrium is considerably soluble. The process is therefore unsuitable for the scandium extraction.

D. 142. Detection of Scandium (P. 142).—It was found that the absence or probable presence of scandium in the acid ammonium fluoride extract could be determined by simply evaporating it with sulfuric acid till this acid fumed strongly and cooling the mixture; for a precipitate of its sulfate separates from the concentrated acid when only 0.5 mg. of scandium is present. This behavior was found to distinguish scandium from zirconium and titanium, but not from other rare-earth elements nor from some of the common elements. A further confirmatory test for scandium was therefore worked out, consisting in a proof that the extracted substance again shows the property, characteristic of scandium, of being precipitated by hydrofluoric acid and then redissolved by acid ammonium fluoride solution.

D. 143. Separation of Indium, Thorium, and Cerium from the Other Rare-Earths (P. 143).—Since, as stated in D. 123, a large proportion of the indium may be carried into the original fluoride precipitate, and since it was found that only little of it is extracted with the scandium by the ammonium fluoride treatment, it is necessary to separate it from the rare-earth elements and detect it. This is readily done at this point by decomposing the fluorides with strong sulfuric acid, precipitating all the elements with ammonium hydroxide, dissolving the precipitate in 6 normal acetic acid, and saturating the solution with hydrogen sulfide; whereupon the indium separates in the form of its bright-yellow sulfide.

For separating thorium from the other rare-earth elements the most suitable method seemed to be the precipitation of thorium by potassium iodate in the presence of fairly strong nitric acid in the way described by R. J. Meyer.[1] The known fact that cerium in the quadrivalent state also forms a slightly soluble iodate suggested that cerium might be precipitated at the same time with thorium, provided it could be completely converted into this iodate in a strongly acid solution. Experiments made with potassium chlorate in strong nitric acid solution showed that this conversion is practicable, and that cerium can then be completely precipitated, together with the thorium.

[1] Meyer, *Z. anorg. Chem.*, 71, 65 (1911).

A series of experiments showed that under the worked-out conditions a precipitate is produced with even 0.5 mg. of thorium or cerium; that at least 100 mg. of either of these elements are completely precipitated; that more than 100 mg. of any of the other rare-earth elements (thus about 120 mg. of lanthanum, about 190 mg. of yttrium, and over 200 mg. of ytterbium), when present alone, remain in the solution; and that, when as little as 1 mg. of these elements is associated with 100 mg. of thorium or cerium, it can be detected in the filtrate from the iodate precipitate. (In this separation, and throughout the analysis of this rare-earth group, it is assumed that there is present in the solution not more than 100 mg. of thorium or cerium or of either of the rare-earth subgroups referred to below.)

Experiments showed that zirconium is completely precipitated as iodate under the same conditions as thorium; but it could hardly be present after the treatments with hydrofluoric acid and ammonium fluoride; and if it were, it would not show the confirmatory test for thorium described below. Scandium was found to be precipitated as iodate only when more than 40 mg. of it are present,—a quantity much larger than that which might possibly fail to be extracted by the ammonium fluoride treatment.

D. 144. Separation of Thorium from Cerium and their Detection (*P. 144–146*).—Having found the iodate method so satisfactory for the separation of thorium and (quadrivalent) cerium from the other rare-earth elements, it seemed simplest to use this same reagent also for separating thorium and cerium from one another, after reducing the cerium to the trivalent state, in which it behaves like lanthanum towards nearly all precipitants. It was found that this reduction could be effected, even without destroying the iodate, by merely heating the precipitate of the two iodates with a mixture of hydrogen peroxide and nitric acid, and adding a little more potassium iodate to the mixture (to ensure the reprecipitation of the small quantity of thorium which dissolves in the nitric acid). It was found by this process that even 100 mg. of cerium as ceric iodate are readily dissolved when present alone, that 1 mg. of cerium is extracted from an iodate precipitate containing 100 mg. of thorium, and that even 1 mg. of thorium in the presence of 100 mg. of cerium gives a distinct precipitate upon the final addition of the potassium iodate reagent.

For the confirmation of the presence of thorium in the second iodate precipitate and for the detection of cerium in the filtrate from it very characteristic tests are available; namely, the precipitation of thorium by hydrogen peroxide in slightly acid solution as described by Wyrouboff and Verneuil,[1] and the well-known precipitation of cerium as yellow or dark-orange ceric peroxyhydroxide by hydrogen peroxide and ammonium hydroxide. These tests detect less than 0.5 mg. of thorium and less than 0.1 mg. of cerium; and in the test for thorium no precipitate is produced even by 50 mg. of zirconium or 100 mg. of cerium.

D. 145. Fractionation of the Rare-Earths (P. 147–148).—The next step in the analysis is to separate the rare-earths roughly into two subgroups,—the *lanthanum subgroup,* consisting of the elements lanthanum, praseodymium, neodymium, samarium, and europium,[2] and the *yttrium subgroup,* consisting of yttrium and of the elements between gadolinium and lutecium inclusive.

Sodium sulfate in concentrated solution is the reagent that has been most commonly employed; but the unsatisfactory separation which this is known to give led us to study in detail two other reagents, which have been previously used for rare-earth fractionations. These are ammonium formate and potassium carbonate. The latter was recommended by Drossbach[3] as one of the best reagents for a rough preliminary separation; the former has recently been studied by Meyer and Müller.[4]

The formate experiments were made by treating in separate experiments known quantities of the dry chlorides of various rare-earth elements with 1½ cc. of 95% $HCHO_2$ and 5 cc. of 6 n. NH_4OH (yielding a mixture roughly 5 normal in ammonium formate and 1 normal in formic acid), heating to boiling, cooling, filtering after 10 minutes, and estimating the quantity of the rare-earth remaining in the filtrate.

The procedure employed in the potassium carbonate experiments was to warm the separate rare-earths in the form of the dry chlorides with 3 cc. of 50% K_2CO_3 solution (in which 100

[1] Wyrouboff and Verneuil, *Bull. soc. chim.* (3), 19, 219 (1898).

[2] The transition element europium, whose behavior was not studied in this investigation, is included in the first subgroup, though it doubtless divides itself between the two subgroups in larger measure than any other element.

[3] Drossbach, *Ber. deutsch. chem. Ges.,* 33, 3506 (1900).

[4] Meyer and Müller, *Z. anorg. Chem.,* 109, 17 (1919).

mg. of any of the elements except lanthanum dissolve completely), add 20 cc. or 25 cc. of water, heat the mixture on a steam-bath for 2 hours, filter, and estimate the rare-earth element remaining in the filtrate. In the experiments 100 mg. of the rare-earth element, or sometimes less of the less soluble ones, were used.

The results of these experiments are here summarized.

Reagent used	Milligrams found in filtrate							
	La	Pr	Nd	Sm	Gd	Er	Yb	Y
1½ cc. 95% $HCHO_2$ and 5 cc. 6 n. NH_4OH	0.3	1.0	1.5	2.5	65	100	100	100
3 cc. of 50% K_2CO_3 and 25 cc. of water	0.3	0.4	4.0	8.5	70	—	95	93
3 cc. of 50% K_2CO_3 and 20 cc. of water	0.3	1.0	4.5	>10	—	—	100	100

In view of the well-known tendency of the more soluble rare-earths to be carried out by the less soluble ones, similar experiments were made with mixtures of 100 mg. of lanthanum with various quantities of other elements. The numbers of milligrams taken and found in the filtrate are shown in the following table:

Reagent used	Element	Gd	Er	Er	Yb	Y	Y	Y
	Taken	8	8	4	4	4	8	50
1½ cc. 95% HCO_2H and 5 cc. 6 n. NH_4OH	Found	0	½	0	½	½	1½	20
3 cc. 50% K_2CO_3 and 25 cc. of water	Found	—	2½	—	—	—	1½	35

It will be seen from these results that with both reagents there is a fairly sharp break in the behavior of the rare-earths, when only a single one is present, in passing from samarium to gadolinium; but that, when a large quantity of lanthanum is present, a large proportion, or even the whole amount, of the yttrium-elements is carried into the precipitate. The results show, moreover, that there is not a very great difference in the effect of the two reagents, but that the carbonate retains in solution more of the yttrium-elements, especially when the reagent is used in its more concentrated state; while the formate precipitates the lanthanum-elements more completely.

These facts led to adoption of the following plan of using the two reagents in succession. In the first place the rare-earth solution is treated with the concentrated carbonate mixture, whereby any large amount of lanthanum-elements present is precipitated, while leaving in the filtrate, with the small remaining quantity of these elements, as large a proportion as possible of the yttrium-elements. Then this mixture of rare-earths is recovered from the filtrate and treated with ammonium formate, whereby the

lanthanum-elements are now almost completely precipitated, leaving the yttrium-elements in a fairly pure state.

The separation by this process of the lanthanum-elements from the yttrium-elements is, of course, very imperfect. Nevertheless, it always enables the presence or absence of lanthanum-elements to be determined and their quantity to be approximately estimated; for the only effect of the presence of even a large quantity of yttrium-elements is to increase somewhat the size of the lanthanum-subgroup precipitate. The process also shows the presence or absence of the yttrium-elements and the approximate quantity present, in any case where there is no precipitate or only a small precipitate of the lanthanum subgroup; but in the case where a large precipitate of this subgroup results the indications as to the yttrium-elements are unreliable, namely in the respects that a small quantity of them, up to say 5 mg., entirely escapes detection, and that any larger quantity may be much underestimated.

It seems probable that a better separation might be secured by using the potassium carbonate in more concentrated form (for example, 3 cc. of 50% K_2CO_3 diluted with only 10 cc. of water); but this was not investigated.

Attempts were also made to effect a separation by using hot concentrated 95% formic acid alone, without addition of ammonium formate; for this treatment had been found to precipitate samarium with remarkable completeness. But the attempts were abandoned, without exhaustive study, because of the existence of an extreme tendency to supersaturation.

D. 146. Partial Separation of Praseodymium and Lanthanum from Neodymium and Samarium by Fusion with Sodium Nitrate (P. 149).—The only possibility of further separating the rare-earths by a simple analytical method seemed to be to make use of the fact that certain of them exist in other than the trivalent state. The elements besides cerium which so exist are praseodymium and terbium, which form on igniting in oxygen black dioxides, and samarium and europium, which, according to Matignon and Cazes[1] and Urbain and Bourion,[2] are reduced to bivalent chlorides ($SmCl_2$ and $EuCl_2$) by ignition of their trivalent chlorides at a very high temperature in hydrogen or ammonia.

[1] Matignon and Cazes, *Compt. rend.*, **142**, 83 (1906); *Ann. chim. phys.*, (8), **8**, 417 (1906).

[2] Urbain and Bourion, *Compt. rend.*, **153**, 1155 (1911).

Not only might these elements thus be isolated, but by their removal there would be produced in the series of rare-earths gaps which might make it possible to secure, by the usual precipitation methods, a tolerable separation of the elements on the two sides of the gap. Thus in the series lanthanum, cerium, praseodymium, neodymium, after cerium and praseodymium were removed by converting them into their higher valence states, lanthanum might be separated from neodymium by a much smaller number of fractionations than would be required if the intermediate elements were present.

In accordance with this idea, an extended investigation was made of the possibility of separating praseodymium from the other elements by converting it into its dioxide. The process employed by Brauner and tested by Meyer [1] of fusing the rare-earth nitrates with an alkali nitrate at 400–450° and extracting the melt with water or ammonium nitrate solution seemed promising for this purpose. It was found, however, as these authors have stated, that under the conditions heretofore employed the separation of praseodymium from lanthanum, especially when a large proportion of the latter is present, is not satisfactory; and a long series of experiments was made in the hope of improving these conditions and thus developing a method by which a fairly complete isolation of the praseodymium could be attained.

Most of the experiments were made by fusing in a covered 30-cc. porcelain crucible 7 g. of sodium nitrate intimately mixed with various known quantities (usually 3 to 100 mg.) of praseodymium, lanthanum, neodymium, or samarium as nitrate, either separately or together, for definite lengths of time, at various definite temperatures. Constant temperature was attained either by placing the crucible in the vertical chamber of a well-insulated electric furnace provided with a copper-constantan junction, or by heating it (at 445°) in a vertical tube within a jacket filled with the vapors of boiling sulfur. After the melt had cooled it was extracted with about 20 cc. of cold water; and any residue was then agitated for 15–30 minutes with 8 cc. of 1 normal $HC_2H_3O_2$ and 40 cc. of 1 normal $NaC_2H_3O_2$ solution. The proportions of the element in the aqueous extract, in the acetate solution, and in the residue (after dissolving it in hydrochloric acid) were estimated by precipitating the hydroxide with ammonium or sodium

[1] Meyer, *Z. anorg. Chem.*, 41, 120 (1904).

hydroxide, and estimating the amount of the precipitates from their appearance, or in a few cases by igniting and weighing them.

The experiments are described in detail among the Confirmatory Experiments. They showed that the results of heating at 460° for 1½ hours are substantially the same as those of heating for 5 hours at 445°, and that apparently the best separation is attained under these conditions. The average results obtained in this way are summarized in the following table, duplicate experiments (with (1), (2), (3) . . . attached) being cited when the check results were widely divergent.

Milligrams taken	Milligrams found in								
	Water extract			Acetate solution			Residue		
	Pr	La	Nd or Sm	Pr	La	Nd or Sm	Pr	La	Nd or Sm
100 Pr (1)	0	—	—	4	—	—	96	—	—
(2)	0	—	—	1	—	—	99	—	—
100 La (1)	—	64	—	—	6	—	—	30[a]	—
(2)	—	82	—	—	10	—	—	8[a]	—
(3)	—	88	—	—	9	—	—	3[a]	—
100 Nd (1)	—	—	20	—	—	80	—	—	0
(2)	—	—	46	—	—	52	—	—	2
100 Sm (1)	—	—	59	—	—	40	—	—	1
(2)	—	—	12	—	—	88	—	—	0
100 Pr + 3 La	0.3	0.7	—	2	0.9	—	98	1.4	—
100 Pr + 10 La	2	8	—	5	0.5	—	93	1.5	—
100 Pr + 6 Nd	0	—	0	2	—	0.8	98	—	5
10 Pr + 100 La	0.5	90	—	9	3	—	0.5	7[a]	—
3 Pr + 100 La (1)	0.1	86	—	2.8	12	—	0.1	2	—
(2)	1.8	89	—	1.0	9	—	0.2	2	—
3 Pr + 100 Nd	1	—	17	2	—	81	0	—	2
50 La + 50 Nd	—	47	28	—	1	21	—	—	—

[a] The lanthanum in the residue was always in the form of lustrous crystalline La_2O_3.

It will be seen from this table that:—

(1) The water extract contains: *a*, little, if any, of the praseodymium, whether it is present alone or with a very large proportion of other elements; *b*, 70–90% of the lanthanum (except that when 3 mg. are present with 100 mg. of praseodymium only 25% (0.7 mg.) of it is found in the water); *c*, 20–45% of the neodymium when present alone or with lanthanum, but none of it when associated with a large proportion of praseodymium, since this carries it almost completely into the residue.

(2) The residue contains: *a*, nearly all the praseodymium, except that when 3–10 mg. of it are associated with 100 mg. of lanthanum or neodymium it passes almost wholly into the acetate

solution; *b*, only 2–8% of the lanthanum (in form of lustrous crystalline La_2O_3) or 2% of the neodymium when present alone, but half of the lanthanum and nearly all of the neodymium when associated with a large proportion of praseodymium.

(3) The acetate solution contains about 10% of the lanthanum and 40–80% of the neodymium and samarium, except when a large proportion of praseodymium is present.

From these statements it will be seen that the fusion method furnishes a means of obtaining (in the aqueous extract) a large part of the lanthanum free from praseodymium and associated with only a moderate proportion of the neodymium and samarium that are present. By precipitating the rare-earths from the water extract and heating the precipitate with potassium carbonate solution, thus repeating the fractionation-process previously employed, it is possible to separate the lanthanum more completely, and to fully establish its presence, as will be described below. The fusion method also makes possible in most cases the detection of praseodymium and a rough estimate of its quantity from the size and color of the residue insoluble in the acetate solution. Only when a small quantity (such as 3–10 mg.) of praseodymium is present with a large quantity (100 mg.) of neodymium or samarium are these indications unreliable. In that case the praseodymium may still be detected in the acetate solution by igniting the precipitate obtained from it and noting the color of the oxides, as described below.

Nevertheless, the effects are somewhat capricious, and the conclusions to be drawn from the observations are complicated. Moreover, the operations involved are time-consuming, and a special apparatus is required for the heating. For these reasons the process is not recommended as an essential part of the scheme of analysis, to be carried out in all cases. The best procedure that could be devised is, however, presented in detail (as P. 149) at the end of the analysis of this rare-earth group; for it will be useful to analysts who wish to secure all the information about the elements present which qualitative analysis can at present afford, and presentation of the extended researches upon which it is based may save much time for future investigators.

D. 147. Separation of Lanthanum from Other Rare-Earth Elements (P. 149).—Since the water-extract of the melt obtained

in the way just described contains only lanthanum and neodymium and higher elements, the intermediate elements cerium and praseodymium in the rare-earth series having been removed, it seemed promising to attempt to separate the lanthanum from the neodymium by the potassium carbonate process described above, modifying it only by appropriately increasing the volume of solution used. Experiments proved in fact that when 20 cc. of 50% K_2CO_3 solution were used and the solution was diluted with an eight-fold volume of water and heated for two hours, lanthanum gave a precipitate when 2 mg. were present, and neodymium remained almost completely in solution when 25 mg. were present, showing that lanthanum can be distinguished from 12 times as large a quantity of neodymium. To be sure, when both of these elements are present in considerable quantity (say 25 mg. of each) a large proportion of the neodymium separates with the lanthanum. Nevertheless, the carbonate treatment aids substantially in establishing the presence of lanthanum and in estimating the quantities of the various elements present.

D. 148. Estimation of Praseodymium from the Brown Color of the Ignited Oxides (P. 149).—In order to detect and estimate approximately the praseodymium where only a little of it is present with much lanthanum or neodymium, in which case it passes mainly into the acetate solution, it is useful to ignite the precipitate obtained by adding ammonium hydroxide to that solution and to note the depth of its brown color, preferably comparing it with that of standard mixtures of the oxide of praseodymium with the oxide of lanthanum or neodymium. This comparison, it is true, is made less significant from a quantitative standpoint by the fact that neodymium reduces much more than lanthanum the brown color given to the mixed oxides by a certain proportion of praseodymium. Nevertheless, this effect is not so great as to destroy the value of the indication.

In spite of the defects of the method described in the preceding paragraphs for detecting lanthanum, praseodymium, and neodymium, it gives, after the analyst has had some experience with known mixtures so as to aid him in interpreting the results, a fair estimate of the proportions of these elements, in most combinations of them. In view of the difficulty of the problem, the method is perhaps as good a one as can be hoped for.

MODIFICATIONS OF THE PROCESS INVESTIGATED

D. 149. Modifications of the Sodium Nitrate Fusion Process for Separating Praseodymium from Lanthanum and Neodymium. —Before the above-described conditions of making the fusion were finally adopted a large number of experiments were carried out with the object of securing a more rapid and complete conversion of the praseodymium into its dioxide, and of reducing the proportion of the lanthanum that is converted into crystalline oxide or basic nitrate, and thus rendered insoluble in water. These experiments will be here briefly described, even though they led to no substantial improvement of the process.

One group of these experiments consisted in bubbling through the fused mass at 445° various oxidizing gases, namely oxygen, nitrous oxide, nitric-acid vapors, and nitrogen tetroxide. The experiments with oxygen showed that its effect was to reduce the time required at 445° for the complete oxidation of 100 mg. of praseodymium from five hours to three hours; but it caused a somewhat larger proportion of the lanthanum (21 mg. instead of 13 mg. out of 100 mg. taken) to be converted into basic nitrate or crystalline oxide, probably owing to the carrying away of the N_2O_5 by the current of gas. With the view of preventing this, experiments were made by passing through the fused mass for 3 hours a current of air which had been charged with nitric-acid vapors by passing it through a gas wash-bottle containing 16 n. HNO_3 kept at 0° or at 20°. This seemed, however, to make little difference in the results. A current of nitrous oxide was then tried; but this had practically the same effect as oxygen. An experiment was made by passing oxygen containing several percent of ozone into a mixture of sodium nitrate and potassium nitrate with praseodymium nitrate in a state of fusion at 235°; but no praseodymium dioxide whatever was formed.

The effect of adding certain solid oxidizing agents to the sodium nitrate fusion was also studied; namely, of silver nitrate, of sodium peroxide, and of bismuth dioxide; but the results were far less satisfactory than with sodium nitrate alone.

The effect of replacing the sodium nitrate by sodium nitrite or by a mixture of sodium perchlorate and chloride, was also tried; but these fluxes proved to be entirely unsuited.

Tabular Outline XII

See page 210.

Procedures and Notes

Procedure 141.—*Extraction of Scandium from the Fluoride Precipitate.*—Transfer the HF precipitate * (P. 131) to a platinum dish, add 10 cc. of 6 n. NH_4OH and 5 cc. of 27 n. HF solution, and heat the mixture nearly to boiling for 2–3 minutes with frequent stirring. Filter the mixture through a filter supported in a bakelite or hard-rubber funnel, collecting the filtrate in a platinum dish.

Treat the filtrate by P. 142. Treat the precipitate by P. 143.

Notes.—1. By the treatment here described 100 mg. of scandium are completely dissolved when present alone; and 1 mg. of it is extracted from a large precipitate of rare-earth fluorides. None of the other rare-earth fluorides are at all soluble in acid NH_4F solution. Those of the nickel group, on the other hand, dissolve readily in it.

2. Of any indium that was carried into the original HF precipitate (in P. 131) only a small proportion is extracted by the acid NH_4F; thus less than 1 mg. out of 4 mg. of indium occluded by 100 mg. of rare-earth element passes into the solution.

Procedure 142.—*Detection of Scandium.*—To the acid NH_4F solution (P. 141) add 4 cc. of 18 n. H_2SO_4, evaporate until the H_2SO_4 begins to fume strongly, and let the mixture stand for 5–10 minutes. (White translucent precipitate, presence of SCANDIUM.) If there is a precipitate, add to the mixture 10 cc. of water, make it alkaline with 6 n. NH_4OH, and filter out and wash the precipitate. Pour two or three times through the filter a 5-cc. portion of 6 n. HCl, evaporate the

* For practice-analyses use a precipitate obtained as follows. Add 0.5 cc. of 27 n. HF and 1 cc. of 6 n. HCl to a mixture of 1 cc. of each of the test-solutions of scandium, indium, thorium, and cerium, and 2 cc. each of those of lanthanum, neodymium, and yttrium, dilute the mixture to 12 cc., heat it to boiling, and filter it. Omit P. 149.

solution just to dryness in a platinum crucible, and add to the residue 4 or 5 drops of water and one drop of 27 n. HF. (White precipitate, presence of SCANDIUM.) If there is a precipitate, add 2–4 cc. of 27 n. HF and twice as many cubic centimeters of 6 n. NH_4OH. (Disappearance of the precipitate, presence of SCANDIUM.)

Notes.—1. In order to decompose ScF_3 completely, the H_2SO_4 must be heated until it begins to fume strongly. This strong heating also diminishes the solubility of $Sc_2(SO_4)_3$ in the concentrated H_2SO_4.

2. If under these conditions there is no separation of a precipitate from the concentrated H_2SO_4, even after cooling and short standing, it shows the absence of scandium, and no further tests for it need be made; for even ½ mg. of it gives an easily recognizable precipitate. (If much titanium were present, this scandium test would be much less delicate. Thus with 100 mg. of Ti 3 mg. of Sc are required to give a precipitate; but little, if any, titanium should be present at this point.) If the mixture be allowed to stand long in the air, the precipitate may disappear, owing to dilution of the H_2SO_4 by the absorption of water from the air. The precipitate has a characteristic translucent granular appearance.

3. The separation of a precipitate from concentrated H_2SO_4 distinguishes scandium from zirconium and titanium, but not from the rare-earth elements, nor from certain common elements. A further confirmatory test is therefore desirable, even though none of these elements is normally present at this point.

4. The confirmatory test for scandium described in the Procedure is based on its unique property of being completely precipitated by a slight excess of HF and of being then redissolved by an acid NH_4F solution. In making the precipitation, in order to secure delicacy, care must be taken to remove nearly all the HCl, not to add much water, and not to use much more HF than corresponds to the scandium present. Two drops of 27 n. HF are enough for 40 mg. of scandium. As to its behavior with HF see also Note 4, P. 131.

Procedure 143.—*Detection of Indium, and Separation of Thorium and Cerium from the Other Rare-Earths.*—Transfer the HF precipitate (P. 141) to a platinum dish or crucible, add 2–4 cc. of 18 n. H_2SO_4, and heat until the H_2SO_4 fumes

strongly. Cool the solution, pour it into 20–30 cc. of water, make it alkaline with 6 n. NH_4OH, and filter it. Reject the filtrate. Wash the precipitate, and dissolve it by pouring repeatedly through the filter a 5-cc. portion of 6 n. $HC_2H_3O_2$. Saturate the solution in a test-tube at 50–60° with H_2S, cork the tube, and let it stand 10 minutes. (Yellow precipitate, presence of INDIUM.) Filter.

Treat the precipitate no further.

Boil the filtrate till the H_2S is expelled, add 2 cc. of 6 n. HNO_3, and evaporate the solution in a casserole just to dryness. Add to the residue 6 cc. of 16 n. HNO_3 and 1 g. of powdered $KClO_3$, and heat the mixture nearly to boiling, preferably on a steam-bath, for 5 minutes, keeping the casserole covered. Add to the solution 20 cc. of 0.35 n. KIO_3, cool it at once to 20–25°, and filter it after 10 minutes. (White precipitate, presence of THORIUM; yellow precipitate, presence of CERIUM.) Wash the precipitate with a little cold water mixed with one tenth its volume of 0.35 n. KIO_3.

Treat the precipitate by P. 144. Treat the filtrate by P. 147.

Notes.—1. After the fluorides have been decomposed by H_2SO_4 the rare-earth elements are precipitated with NH_4OH to separate them from the excess of sulfate present, and to enable indium to be tested for. If alkaline-earth elements should be present in the fluoride precipitate, they will also be separated from the rare-earth elements by this NH_4OH precipitation.

2. Since indium may be carried down almost completely by the rare-earths in the original HF precipitation (see Note 5, P. 131), it has to be tested for in the analysis of this group, and this is done most simply at this point in the way indicated. Even 200 mg. of the rare-earth elements dissolve in 5 cc. of 6 n. $HC_2H_3O_2$, and their solution is not affected by H_2S.

3. Cerium is completely oxidized to the ceric state by heating with $HClO_3$ and 16 n. HNO_3 for 5 minutes on a steam-bath. If the heating be much longer continued or if the mixture be boiled, the $HClO_3$ is expelled from the solution and partial reduction of the cerium may take place.

4. The iodate of thorium is slightly soluble, and that of quadrivalent cerium is considerably soluble, in strong HNO_3; hence,

in order to secure complete precipitation of these elements, the prescribed excess of the KIO_3 reagent must be added. As the ceric iodate is slightly soluble even in cold water, the precipitate is washed with water to which KIO_3 reagent has been added.

5. By following the directions given in this Procedure a precipitate is obtained with even 0.5 mg. of thorium or cerium; 100 mg. of either of these elements are completely precipitated; even 100 mg. of any other rare-earth element give no precipitate; and even 1 mg. of any other rare-earth element when associated with 100 mg. of thorium and cerium passes into the filtrate in detectable quantity.

6. In general, throughout this analysis of the rare-earth group, the fact should be borne in mind that the directions have been worked out for the case that there are present not more than 100 mg. of any one element or subgroup, thus of thorium, cerium, the lanthanum subgroup, or the yttrium subgroup. In case more of any of these seems to be present, a due fraction of the HNO_3 solution, instead of the whole, should be subjected to the analysis.

Procedure 144.—*Separation of Thorium from Cerium.*—Rinse the KIO_3 precipitate (P. 143) into a conical flask with 1 f. H_2O_2, using according to the size of the precipitate just 18 cc. or just 35 cc. of this reagent; add just 5 cc. or just 10 cc. of 16 n. HNO_3, and heat the mixture nearly to boiling for 5 minutes. Add just 10 cc. or just 20 cc. of 0.35 n. KIO_3, cool the mixture, and let it stand. (White precipitate, presence of THORIUM.) Filter after 10 minutes, and wash the precipitate with cold water to which one tenth its volume of 0.35 n. KIO_3 solution has been added.

Treat the precipitate by P. 145. Treat the filtrate by P. 146.

Notes.—1. By heating with H_2O_2 solution and HNO_3 the slightly soluble $Ce(IO_3)_4$ is completely reduced to the readily soluble $Ce(IO_3)_3$. Some $Th(IO_3)_4$ is at the same time dissolved by the HNO_3; but this reprecipitates on adding the KIO_3 solution and letting the mixture stand for 10 minutes. It should not stand much longer, since some cerium may then precipitate.

2. In order to secure complete precipitation of the thorium, the concentrations of the HNO_3 and KIO_3 in the mixture must conform closely to those given in the Procedure. The prescribed *proportions* of the three reagents must therefore be adhered to,

but a smaller or larger *volume* of each may be used according to the size of the original iodate precipitate. Even with the larger volume 1 mg. of thorium is readily detected in the presence of 100 mg. of cerium.

3. When only a little cerium is present with much thorium it is necessary to heat the precipitate of the two iodates with the H_2O_2 and HNO_3 for several minutes before adding the excess of KIO_3; for otherwise the cerium will be extracted only very incompletely. When this precaution is observed, 1 mg. of cerium can be separated from 100 mg. of thorium, and can be subsequently detected in the confirmatory test in P. 146.

Procedure 145.—*Confirmation of Thorium.*—Dissolve the KIO_3 precipitate (P. 144) by pouring repeatedly through the filter a hot 5–10 cc. portion of 6 n. HCl. Evaporate the solution just to dryness, moisten the residue with 12 n. HCl, and evaporate on a steam-bath until the hot residue no longer smells of HCl. Add 2 cc. of water, 2 drops of 6 n. HCl, and 5 cc. of 1 f. H_2O_2; pour the mixture into a test-tube, and heat it for 5–10 minutes in a beaker of water at 60–70°. (White flocculent precipitate, presence of THORIUM.)

Notes.—1. The repeated evaporations with concentrated HCl reduce the iodate and enable the thorium to dissolve as chloride. In order to detect a small quantity of thorium, care must be taken to evaporate until the residue has not even a slight acid odor, and then to add only two drops of 6 n. HCl. This small quantity of acid is added to avoid the possibility of precipitating cerium or other rare-earth element.

2. Under the prescribed conditions 0.5 mg. of thorium gives a precipitate of $ThO_2 \cdot H_2O_2$ (thorium peroxyhydroxide); and at least 100 mg. of cerium or 50 mg. of zirconium remain in solution.

Procedure 146.—*Confirmation of Cerium.*—Make the filtrate from the KIO_3 precipitate (P. 144) alkaline with 6 n. NH_4OH, and heat it to boiling. (Yellow or orange flocculent precipitate, presence of CERIUM.)

Notes.—1. The yellow or orange color of the precipitate of $CeO_2 \cdot H_2O_2$ (cerium peroxyhydroxide) produced by NH_4OH and H_2O_2 is highly characteristic. The test is, moreover, so delicate that a bright-yellow precipitate is produced with even less than 0.2 mg. of cerium.

FRACTIONATION OF RARE-EARTH ELEMENTS

Procedure 147.—*Fractionation of the Rare-Earths by Potassium Carbonate.*—Make the filtrate from the KIO_3 precipitate (P. 143) slightly alkaline with 6 n. NH_4OH. (Precipitate, presence of RARE-EARTH ELEMENTS.) Filter. Reject the filtrate. Wash the precipitate, and dissolve it by pouring repeatedly through the filter a 5–10 cc. portion of 6 n. HCl. Evaporate the solution just to dryness. Moisten the residue with 12 n. HCl, and evaporate to dryness, preferably on a steam-bath, continuing the heating till the hot residue has no acid odor. To the residue add from a graduated pipet just 3 cc. of 50% K_2CO_3 solution. Warm the mixture to dissolve the residue, rinse the solution with just 20 cc. of water into a 30-cc. nickel crucible, cover the crucible with a closely fitting cover, and heat it for two hours on a steam-bath, replacing from time to time any water that may have evaporated, but taking care not to add more than this. (Flocculent precipitate, presence of LANTHANUM SUBGROUP.) Filter, wash the precipitate with a very little water.

Dissolve the precipitate by pouring repeatedly through the filter a 5–10 cc. portion of 6 n. HNO_3. Dilute the solution with water to 25 cc., make it alkaline with 6 n. NH_4OH, and heat it nearly to boiling. (Precipitate, presence of LANTHANUM SUBGROUP.) Keep the mixture, and unite it with the lanthanum subgroup precipitate obtained in P. 148.

Acidify the filtrate from the K_2CO_3 precipitate with 6 n. HCl, boil it till the CO_2 is expelled, and make it alkaline with 6 n. NH_4OH. (White or reddish-white precipitate, presence of YTTRIUM SUBGROUP, NEODYMIUM, or SAMARIUM.) Compare the size of the precipitate with that of the NH_4OH precipitate of the lanthanum subgroup. Filter out and wash the precipitate, rejecting the filtrate. Treat the precipitate by P. 148.

Notes.—1. Since the first NH_4OH precipitate contains some iodate, the solution of it in HCl is evaporated a second time with 12 n. HCl to reduce the iodate completely.

2. The purpose of this K_2CO_3 treatment is to effect a rough separation of the *lanthanum subgroup* (consisting of lanthanum, praseodymium, neodymium, samarium, and europium) from the *yttrium subgroup* (consisting of yttrium and the rare-earths from gadolinium to lutecium inclusive, atomic nos. 64 to 71). The reagent K_2CO_3 is chosen and its concentration is adjusted so as to favor non-precipitation of the yttrium subgroup, even at the expense of not throwing down all of the lanthanum subgroup. Provision is then made, in the next procedure, for precipitating most of the remainder of the lanthanum subgroup by using a reagent, NH_4CHO_2, more effective in this respect; for, though this has also a greater tendency to precipitate the yttrium subgroup, yet little of the latter can be carried out by the small quantity of lanthanum subgroup left in solution after the K_2CO_3 treatment.

3. The results of this fractionation are greatly influenced by the concentration of the K_2CO_3 solution. The volume of the 50% K_2CO_3 reagent and that of the water are therefore accurately measured. If the K_2CO_3 is more concentrated than that recommended, a larger quantity of the lanthanum subgroup remains in solution; if less concentrated, the yttrium subgroup is carried down in larger proportion, or may even precipitate when present alone in large quantity.

4. Long heating at nearly 100° makes the precipitation of the lanthanum subgroup more complete. This heating is carried out in a nickel crucible, rather than in a glass or porcelain vessel, since in the latter case a considerable precipitate results from the action of the reagent upon the vessel.

5. Under the conditions of the Procedure the quantities of elements of the lanthanum subgroup which when present alone remain in solution are roughly 0.3 mg. of lanthanum, 1.0 mg. of praseodymium, 5 mg. of neodymium, and more than 10 mg. of samarium and europium; while at least 70 mg. of gadolinium and 100 mg. of ytterbium or yttrium remain in solution. When, however, a large lanthanum-subgroup precipitate results, a large proportion of the yttrium elements may be contained in it; thus the precipitate produced from a solution of 100 mg. of lanthanum and 8 or 50 mg. of yttrium may contain, along with all the lanthanum, 6 or 15 mg., respectively, of the yttrium.

6. Therefore, non-formation of a K_2CO_3 precipitate shows the absence of lanthanum and praseodymium, also of neodymium in excess of 5 mg.; but not of samarium or europium. Formation of a precipitate shows the presence of one or more of these ele-

ments. Formation of a precipitate with NH_4OH in the acidified filtrate from the K_2CO_3 precipitate shows the presence of the yttrium subgroup or of samarium or europium, provided it corresponds to more than 5 mg. of rare-earth element; if smaller than this, it may also be due to neodymium. Non-formation of a precipitate shows the absence of all these elements only in case the lanthanum-subgroup precipitate is small.

7. The lanthanum-subgroup precipitate produced by K_2CO_3 is redissolved, and the rare-earth in it precipitated by NH_4OH, so that the size of the precipitate may be directly compared with that of the precipitate of the yttrium subgroup produced by NH_4OH under similar conditions. In this way a first approximation may sometimes be made of the proportion in which the elements of the two subgroups are present in the material analyzed; but the facts must be taken into account that a considerable part (perhaps one fourth) of the lanthanum-subgroup precipitate may consist of yttrium subgroup, and that a large part of the whole of a small yttrium-subgroup precipitate may consist of neodymium, samarium, or europium. A much more conclusive estimate can, however, be made after the second fractionation in P. 148.

Procedure 148.—*Fractionation of the Rare-Earths by Ammonium Formate.*—Dissolve the yttrium-subgroup precipitate (P. 147) by pouring repeatedly through the filter a 5–10 cc. portion of 6 n. HCl. Evaporate the solution just to dryness, and heat it on a steam-bath till it no longer smells of acid. To the dry residue add from a graduated pipette just 1.5 cc. of 90% $HCHO_2$ (s. g., 1.20). Agitate to dissolve the residue, add just 5 cc. of 6 n. NH_4OH, transfer the mixture to a test-tube, heat it nearly to boiling, cool it, and let it stand for 10 minutes with frequent shaking. (Crystalline precipitate, presence of NEODYMIUM, SAMARIUM, or EUROPIUM.) Filter through a 5-cm. hardened filter-paper, and wash the precipitate once with a mixture of 0.3 cc. of 90% $HCHO_2$ and 1 cc. of 6 n. NH_4OH.

Dissolve the precipitate by pouring repeatedly through the filter a 5–10 cc. portion of 6 n. HNO_3. Dilute the solution with water to 25 cc., make it alkaline with 6 n. NH_4OH, and heat it nearly to boiling. Unite the mixture with that containing the lanthanum-subgroup precipitate obtained in P. 147.

(Precipitate, LANTHANUM SUBGROUP.) Treat the united mixtures by P. 149.

Dilute the filtrate from the NH_4CHO_2 precipitate with water to 25 cc., make it alkaline with 6 n. NH_4OH, and heat it nearly to boiling. (White or reddish-white precipitate, presence of YTTRIUM SUBGROUP.) Compare the size of the precipitate with that of the united NH_4OH precipitates of the lanthanum subgroup. Treat it no further.

Notes.—1. The quantities of $HCHO_2$ and NH_4OH here recommended must be closely adhered to, since it is essential that the NH_4CHO_2 be concentrated, that the mixture be distinctly acid with $HCHO_2$, and that the total volume be not much larger than 6½ cc. The solution is heated nearly to boiling as this lessens the tendency of the formates of the lanthanum subgroup to remain in supersaturated solution.

2. Even 100 mg. of any rare-earth element dissolve in 1.5 cc. of 90% $HCHO_2$ upon agitation or slight warming; but upon heating to boiling a large precipitate separates. For this reason, and also for the sake of avoiding evaporation of the $HCHO_2$, the mixture should not be heated, at any rate to more than 50°, before the addition of the NH_4OH.

3. Under the conditions of the Procedure the quantities of the elements of the lanthanum subgroup which when present alone remain in solution are roughly 0.3 mg. of lanthanum, 0.5 mg. of praseodymium, 1½ mg. of neodymium, and 3 mg. of samarium; while 65 mg. of gadolinium and over 100 mg. of other elements of the yttrium subgroup remain in solution. The latter elements are again carried down to some extent in the lanthanum-subgroup precipitate; but, since any large quantity of this subgroup originally present was removed by the K_2CO_3 treatment (in P. 147), the precipitate here formed cannot be large, and hence will not occlude much of the yttrium subgroup. If the whole quantity of the rare-earths had been directly subjected to this Procedure, the yttrium subgroup would, in case a large quantity of the lanthanum subgroup were present, be carried into the NH_4CHO_2 precipitate in even larger proportion than into the K_2CO_3 precipitate; thus the NH_4CHO_2 precipitate from a solution of 100 mg. of lanthanum and 50 mg. of yttrium contains all the lanthanum and 30 mg. of the yttrium, and that from a solution of 100 mg. of lanthanum and 4 mg. of yttrium or of ytterbium contains all but 0.5 mg. of the yttrium or ytterbium.

4. Hence the following conclusions may be drawn from the results. Non-formation of a precipitate either with NH_4CHO_2 or K_2CO_3 shows the absence of all elements of the lanthanum subgroup, except that 3 mg. of samarium and a larger quantity of europium may remain in solution (though probably only when other elements of this subgroup are not present). Formation of a precipitate with NH_4CHO_2 shows the presence of neodymium, samarium, or europium (since lanthanum and praseodymium are removed by the K_2CO_3 treatment). Production of a considerable precipitate by NH_4OH in the filtrate from the NH_4CHO_2 precipitate shows the presence of the yttrium subgroup; that of a small precipitate, the presence either of this subgroup or of samarium or europium. Non-formation of any such precipitate shows the absence of the yttrium subgroup in case the united precipitates of the lanthanum subgroup are small; and in this case the sizes of the precipitates of the two subgroups afford a reliable measure of the quantities of the elements of those subgroups actually present. In case the lanthanum-subgroup precipitates are large, however, the true quantity present of the elements of the lanthanum subgroup may be considerably (perhaps one fourth or one third) less than the size of the precipitates indicates, and the true quantity of the yttrium-subgroup elements may be correspondingly greater.

Procedure 149.—*Partial Separation of Lanthanum, Praseodymium, Neodymium, and Samarium by Nitrate Fusion.**—Collect the united lanthanum-subgroup precipitates (P. 148) on a single filter; dissolve them by pouring repeatedly through the filter a 5–10 cc. portion of 6 n. HNO_3; and evaporate the solution to dryness in a 30-cc. porcelain crucible. To the residue add 2 drops of 6 n. HNO_3 and 2–3 drops of water; then add 7 g. of finely crystalline $NaNO_3$, and stir so as to produce an intimate mixture. Cover the crucible, and heat it for 5 hours in the vapors of boiling sulfur (see Note 4). Let the crucible cool, nearly fill it with cold water, and stir the mixture occasionally in the cold till the $NaNO_3$ has dissolved. Filter the mixture through a 5-cm. filter-paper. Treat the solution as described in the next paragraph. Wash the residue

* It is recommended that this time-consuming Procedure be omitted by students, and by analysts who do not need the additional information it affords. See Note 1.

thoroughly with cold water. Rinse it into a flask with a mixture of 20 cc. of 1 n. $NaC_2H_3O_2$ and 4 cc. of 1 n. $HC_2H_3O_2$, shake the mixture occasionally for ten minutes, and filter it through a 5-cm. filter. (Black or chocolate-brown residue, presence of PRASEODYMIUM.) Treat the acetate solution as described in the next to last paragraph, and the residue as described in the last paragraph, of this Procedure.

Make the aqueous solution of the $NaNO_3$ fusion slightly alkaline with 6 n. NH_4OH, and filter it, rejecting the filtrate. Wash the precipitate; dissolve the whole of it if it is small, or that quantity of it which contains about 30 mg. of rare-earth elements if it is large, in as many cubic centimeters of 50% K_2CO_3 solution as there seem to be milligrams of rare-earth element in the precipitate taken; add eight times the volume of water, and heat the mixture in covered nickel crucibles or platinum dishes on a steam-bath for two hours, replacing from time to time any water that has evaporated. (White flocculent precipitate, presence of LANTHANUM.) Filter. Wash the precipitate, ignite it in a porcelain crucible, and add to the residue two drops of 6 n. HNO_3. (White residue and colorless solution, confirmation of LANTHANUM.) Treat this solution no further. Acidify the filtrate with 6 n. HCl, boil it till the CO_2 is expelled, and make it alkaline with 6 n. NH_4OH. (Precipitate, presence of NEODYMIUM, SAMARIUM, or YTTRIUM SUBGROUP.)

Make the acetate solution alkaline with 6 n. NH_4OH. (Precipitate, presence of RARE-EARTH ELEMENTS.) In case the residue from the acetate treatment was dark-colored, treat this mixture no further. Otherwise, filter this mixture through a HF-washed filter. Reject the filtrate. Wash the precipitate, and transfer it with the filter-paper to a 30-cc. porcelain crucible. Ignite the open crucible in an inclined position at a moderate temperature till the paper is completely incinerated. (Chocolate-brown residue, presence of PRASEODYMIUM.) Compare the color of this residue with that of standard mixtures (see Note 13).

Treat the residue from the treatment with the acetate solution no further, in case it was very dark-colored. Otherwise dissolve it by pouring repeatedly through the filter containing it a 5-cc. portion of 6 n. HCl. Add to the solution 5 cc. of water and enough 6 n. NH_4OH to make it alkaline. (Light-green flocculent precipitate, presence of PRASEODYMIUM.) Filter out and wash the precipitate, and ignite it as described in the preceding paragraph. (Chocolate-brown residue, presence of PRASEODYMIUM.)

Notes.—1. This Procedure does not give sharp separations nor lead to fully conclusive results. It is recommended that it be carried out only when it is thought worth while to obtain all the indications as to the quantities of the different rare-earths present which a qualitative analysis of the chemical type can afford. The most definite conclusions to be drawn are as to whether each of the two elements lanthanum and praseodymium is present in small or in predominating proportion.

2. The differentiation of the elements is based primarily on the facts that by long fusion with $NaNO_3$ at 445° praseodymium is converted into a higher oxide PrO_2, which dissolves only slightly if at all upon treatment of the melt with water and with acid $NaC_2H_3O_2$ solution, while lanthanum is transformed mostly into neutral nitrate which dissolves in the water, and neodymium and samarium are changed into basic nitrates which dissolve partly in the water, but mainly in the acid $NaC_2H_3O_2$ solution. The differentiation depends secondarily on the fact that the lanthanum in the aqueous extract, now no longer associated with praseodymium, can be distinguished from neodymium and rare-earths of higher atomic numbers by its being alone precipitated upon heating with a sufficiently large volume of dilute K_2CO_3 solution.

3. The time of heating the $NaNO_3$ mixture must be adjusted so as to correspond with the temperature. A suitable constant temperature is most readily attained by heating the crucible in the vapors of boiling sulfur (at 445°). The heating must then be continued for 5 hours. If the mixture be heated for a shorter time, some of the praseodymium may fail to be converted into the dioxide, and may pass in part into the aqueous extract of the melt; if for a longer time, the lanthanum is converted to a greater extent into basic nitrate or into a lustrous crystalline oxide, and therefore passes less completely into the aqueous extract.

4. A convenient sulfur-vapor bath for heating the crucible may be readily made out of two cast-iron pipes—one 8 cm. in bore and 36 cm. in length, and the other 5 cm. in bore and 25 cm. in length. On one end of each of these pipes a thread is turned, and an iron cap screwed tightly on with the aid of red lead. On the other end of the smaller pipe a collar is screwed, which serves to support this pipe when it is set into the larger one. The sides of the outer pipe, except for a length of about 4 cm. at the top, are covered with a layer of insulating material at least 3 cm. thick. Solid sulfur about 1 cm. deep is placed in the outer pipe, and this is heated sufficiently to cause a little of the sulfur vapor to escape and burn continuously with a small blue flame at the top of the apparatus just below the collar of the smaller pipe. The crucible is inserted in the inner pipe about 4 cm. from the bottom upon a copper-wire frame; and the top of that pipe is closed with a plug made of a roll of asbestos paper.

5. The fused mass is extracted with cold water, in order to avoid the danger of decomposing some of the PrO_2 by the action upon it of the hot solution which contains some $NaNO_2$ coming from the reduction of the $NaNO_3$ during the fusion. The residue undissolved by water is treated with a solution of $NaC_2H_3O_2$ and $HC_2H_3O_2$; for this solution, which has a very small hydrogen-ion concentration, serves to dissolve the basic nitrates of lanthanum, neodymium, and samarium, without affecting the praseodymium dioxide.

6. Under the prescribed conditions of this Procedure the elements of the lanthanum subgroup behave as follows. *Praseodymium* passes into the aqueous extract of the melt scarcely at all, whether it be present in small or large quantity, alone or with other elements. When it is present in predominating proportion, it is found almost wholly in the residue from the treatment with the acetate solution; but when it is present in small proportion with a large quantity of lanthanum, neodymium, or samarium, it may pass entirely into the acetate solution. *Lanthanum,* when present in predominating proportion, passes into the aqueous extract to an extent of 70–90%, the remainder being left in the state of a flocculent precipitate which dissolves in the acetate solution, or in the state of crystals of silky luster which remain in the final residue. When present in small quantity (3–6 mg.) together with a large quantity (100 mg.) of praseodymium, 20–40% of it passes into the aqueous extract, the remainder being found in the final residue, intimately mixed or combined with the praseo-

dymium. When roughly equal quantities of the two elements are present, the lanthanum divides nearly equally between the aqueous extract and residue from it, causing the latter to appear of a brown, rather than a black color. *Neodymium* or *samarium,* when present in large quantity, either alone or with lanthanum, divides itself not far from equally between the aqueous extract and the acetate solution. When present in small quantity together with a large quantity of praseodymium, it remains almost wholly in the residue from the acetate solution.

7. From the facts just stated the following conclusions as to praseodymium may be drawn. When after the treatment with acetate solution there is a black, dark-brown, or light-brown residue, praseodymium is present in quantity at least as large as that corresponding to the size and color of the residue; when there is no residue or only a fairly small white residue, a larger quantity of praseodymium than 3–5 mg. is not present, and even this quantity is not present except in case a large precipitate is subsequently obtained from the acetate solution. In this latter case, the fact that there is no dark residue does not prove that a little praseodymium is not present, and the size of a dark residue may be much smaller than corresponds to the amount of praseodymium actually present.

8. Modifications of the fusion process by passing O_2, N_2O, or air charged with HNO_3 vapors through the melt, or by adding $AgNO_3$, Na_2O_2, or BiO_2 to the melt, or by replacing the $NaNO_3$ flux by $NaNO_2$ or $NaClO_4$ and NaCl, lead to results which are little, if any, better, or which are in some cases even much less satisfactory.

9. In the treatment with K_2CO_3 solution, in case the elements are present alone, lanthanum gives a precipitate when not less than 1 mg. of it is present for each 10 cc. of 50% K_2CO_3 solution used; and neodymium remains in solution up to 12 mg. for each 10 cc. of that solution used. The simultaneous presence of lanthanum with this quantity of neodymium gives rise to a small precipitate (containing some neodymium) even when the quantity of lanthanum is less than 1 mg. per 10 cc. of 50% K_2CO_3 used, and to a large precipitate that contains a considerable proportion of neodymium when 10 mg. of lanthanum per 10 cc. are present. By taking these facts into account proper conclusions can be drawn from the formation and size of the precipitate as to the presence and approximate quantity of lanthanum.

10. The ignition of the K_2CO_3 precipitate and dissolving of the

ignited mass in a little acid confirm the presence of lanthanum by showing that an amount of praseodymium or neodymium corresponding to the quantity of the precipitate is not present in it. Praseodymium, if present, imparts a brown color to the ignited mass and a green color to the solution; neodymium, if present, gives a violet color to the solution.

11. The formation by NH_4OH of a precipitate in the acidified filtrate from the K_2CO_3 precipitate shows the presence of neodymium, samarium, or of yttrium elements, since it cannot now arise from praseodymium or lanthanum. The quantity of neodymium present in the material analyzed may, however, be much greater than corresponds to this precipitate, since it is carried down by lanthanum into the K_2CO_3 precipitate, and since the larger part of it is usually found in the acetate solution of the melt, not in the aqueous extract. The precipitate may be treated by P. 148 to show that it does not consist wholly of yttrium-elements in any case where this seems possible.

12. Since the acetate solution of the melt may contain a large proportion of any of the elements originally precipitated by K_2CO_3 and NH_4CHO_2 in P. 147 and 148, the precipitate produced in it by NH_4OH does not throw much further light on the relative quantities of them present. In case, however, the color of the residue from the acetate treatment does not clearly show the presence of praseodymium, the ignition test is applied to this NH_4OH precipitate, so as to detect this element in case it passed entirely into the acetate solution. The ignition test is also applied to the residue from the treatment with the acetate solution in any doubtful case, so as to confirm the presence of praseodymium and afford an estimate of the proportion of it present.

13. The ignited oxide has a grayish-black color when it is pure PrO_2, a white color when it is pure La_2O_3, and a bluish-white color when it is pure Nd_2O_3. It has a color nearly identical with that of (Baker's) powdered cocoa when it contains 25% of praseodymium and 75% of lanthanum, and a color like that of an intimate mixture of 10 volume-percent of cocoa with 90 volume-percent of powdered NaCl when it contains 5% of praseodymium and 95% of lanthanum. The most satisfactory method of comparison, however, is to use a set of standards made by igniting the NH_4OH precipitates from mixtures with known proportions of praseodymium and lanthanum.

ANALYSIS OF THE ALKALINE-EARTH GROUP

Tabular Outline XIII

ANALYSIS OF THE ALKALINE-EARTH GROUP

Ammonium carbonate precipitate (P. 151):
$BaCO_3$, $SrCO_3$, $CaCO_3$, $MgCO_3$.$(NH_4)_2CO_3$.
Dissolve in $HC_2H_3O_2$, add $NH_4C_2H_3O_2$ and K_2CrO_4 (P. 152).

Precipitate: $BaCrO_4$. *Dissolve in HCl, evaporate, add $HC_2H_3O_2$, $NH_4C_2H_3O_2$, and K_2CrO_4 (P. 153).*	Filtrate. *Add NH_4OH and C_2H_5OH (P. 154).*		Filtrate: Ca and Mg salts. *Add $K_2C_2O_4$ (P. 156).*	
	Precipitate: $SrCrO_4$, §$CaCrO_4$. *Boil with $(NH_4)_2CO_3$ and $K_2C_2O_4$ (P. 155).*		Precipitate: CaC_2O_4, §MgC_2O_4. *Treat with H_2SO_4.*	Filtrate: Mg salts. *Add Na_2HPO_4 (P. 158).*
	Residue: $SrCO_3$, CaC_2O_4. *Treat with $HC_2H_3O_2$.*		Solution: $CaSO_4$, $MgSO_4$. *Add C_2H_5OH (P. 157).*	Precipitate: $MgNH_4PO_4$.
Precipitate: $BaCrO_4$.	Solution: $Sr(C_2H_3O_2)_2$. *Add Na_2SO_4.*	Residue: CaC_2O_4.	Precipitate: $CaSO_4$.	
	Precipitate: $SrSO_4$.			

§ This substance may precipitate when a very large quantity of the alkaline-earth element is present.

General Discussion

D. 151. Analysis of the Alkaline-Earth Group.—The process here employed is based upon the one originally described by Bray,[1] and is almost the same as that given in A. A. Noyes' Qualitative Chemical Analysis. The only feature that requires mention is that in this rare-element System of Analysis the solution contains perchlorate, owing to the use of perchloric acid in preparing the solution, and that this, if not removed, would cause potassium, rubidium, and cesium to precipitate with the alkaline-earth group on the addition of ammonium carbonate and alcohol. Fortunately, however, it was discovered that by simply evaporating the solution and igniting the residue most of the perchlorate is destroyed as a result of its reaction with the ammonium salt which is also present in the solution.

[1] Bray, *J. Am. Chem. Soc.*, 31, 611 (1909).

Procedures and Notes

Procedure 151.—*Precipitation of the Alkaline-Earth Group.* —Evaporate the $(NH_4)_2S$ filtrate (P. 96) in a casserole to a small volume over a flame till the separation of salts causes serious bumping, then on a steam-bath to complete dryness. Now continue the heating by causing a flame to play upon the surface of the residue in the casserole, till fumes no longer come off and no part of the residue can still be made to glow. Cool the dish, moisten the residue with 1.0 cc. of 3 n. NH_4Cl, and again evaporate and ignite moderately over a flame till fuming ceases, keeping the dish in motion. Cool the dish, add 10 cc. of water, heat the mixture to boiling, and filter out any undissolved residue.

To the solution add 15 cc. of 6 n. $(NH_4)_2CO_3$ reagent and 15 cc. of 95% C_2H_5OH. If a large precipitate results, add 15 cc. more of each of these liquids. Shake the mixture continuously for 10 minutes; or better, let it stand, with frequent shaking, for at least half an hour. (Precipitate, presence of ALKALINE-EARTH ELEMENTS.) Filter, and wash the precipitate with a little $(NH_4)_2CO_3$ reagent, using suction if the precipitate is large.

Treat the precipitate by P. 152. Treat the filtrate by P. 161.

Notes.—1. The $(NH_4)_2S$ filtrate is evaporated to complete dryness and ignited to destroy the perchlorate. For upon the addition of $(NH_4)_2CO_3$ and C_2H_5OH, the perchlorate, if not removed, would give rise to precipitation of the perchlorate of potassium, rubidium, or cesium when much of these elements is present.

2. The perchlorate is decomposed by reacting with the ammonium salts. When moderately ignited the mixture of these substances reacts vigorously, but not explosively. The decomposition starts at isolated points and spreads through the mixture, raising it locally to incandescence. For this reason the decomposition can be brought about with less heating by causing the flame to play directly onto the residue; but care must be taken that no part of the residue escapes ignition. The residue is moistened with 3 n. NH_4Cl and again ignited, in order to insure complete destruction of the perchlorate.

3. The residue should not be strongly ignited, since the chlorides of the alkali elements are appreciably volatile at a red heat. But when the operations are carried out as directed, even 1 mg. of cesium, the alkali element that forms the most volatile chloride, can be detected in the residue.

4. The $(NH_4)_2CO_3$ reagent used is concentrated, it is added to a small volume (10 cc.) of the aqueous solution, an equal volume of C_2H_5OH is added, and the mixture is allowed to stand in the cold with frequent shaking, in order to ensure the rapid and complete precipitation of the alkaline-earth group, especially of magnesium. For this element is precipitated as the crystalline double carbonate, $MgCO_3 \cdot (NH_4)_2CO_3 \cdot 4H_2O$, which is fairly soluble in cold water, and more so in hot water. Under these conditions less than 0.5 mg. of any of the elements, even of magnesium, remains in solution, whether the quantity present be large or small.

5. Under the conditions of the Procedure, none of the elements of the alkali group is precipitated in appreciable quantity, unless an unusually large quantity is present. Thus, even lithium, whose carbonate is by far the least soluble, remains in solution unless more than 150 mg. is present; and of potassium, which forms with magnesium a double carbonate analogous to that formed by ammonium, less than 1% of that present is carried out.

6. As the precipitated carbonates are somewhat soluble in water, and as alkali-group elements (even lithium) do not interfere with the analysis of the alkaline-earth group, the $(NH_4)_2CO_3$ precipitate is washed not at all with water and only with a little of the cold $(NH_4)_2CO_3$ reagent.

7. The $(NH_4)_2CO_3$ reagent is so prepared as to be about 6 n. in carbonate, and about 9 n. in ammonium. It is made from the commercial solid carbonate, which contains ammonium hydrocarbonate and ammonium carbamate approximately in the proportion shown by the formula $NH_4HCO_3 \cdot CO(NH_2)ONH_4$; but in the solution the carbamate is rapidly converted into $(NH_4)_2CO_3$. The reagent is made up with water containing much NH_4OH, rather than with pure water, so as to reduce the hydrolysis of the carbonate and thus increase the concentration of carbonate-ion.

Procedure 152.—*Precipitation of Barium.*—Pour repeatedly through the filter containing the $(NH_4)_2CO_3$ precipitate (P. 151) a 5–15 cc. portion of hot 6 n. $HC_2H_3O_2$, and evaporate the solution to dryness, taking care not to ignite the residue.

Add to the residue 2 cc. of 6 n. $HC_2H_3O_2$, 10 cc. of 3 n. $NH_4C_2H_3O_2$, and 10 cc. of water, and heat the mixture nearly to boiling in a flask. Add to it just 3 cc. of 3 n. K_2CrO_4, five drops at a time, shaking after each addition, and heat the mixture nearly to boiling for 5 minutes, with frequent shaking. (Yellow precipitate, presence of BARIUM.) In case much precipitate forms, add 2 cc. more of the K_2CrO_4 solution, and heat and shake the mixture. Filter, even though the solution appear clear; and wash the precipitate with a little water.

Treat the filtrate by P. 154.

Treat the precipitate by P. 153, in case in P. 154 much strontium is found present.

Notes.—1. The difference in the solubilities of $BaCrO_4$ and $SrCrO_4$ is so great that under the conditions of the Procedure 0.5 mg. of barium can be detected, while 500 mg. of strontium give no precipitate, even when 5 cc. of 3 n. K_2CrO_4 have been added.

2. In case a large quantity of barium is present, a second portion of the K_2CrO_4 reagent is added; for though the quantity of K_2CrO_4 present in the 3 cc. first added is equivalent to about 600 mg. of barium, yet the excess left in the solution when much barium is present may be so small as not to precipitate it completely. A larger amount of K_2CrO_4 is not added at first, and it is not added at all unless the presence of much barium makes it necessary, since it would increase the tendency of strontium (and in P. 154 of calcium) to precipitate.

3. Acetic acid is added to increase the solubility of $SrCrO_4$. The K_2CrO_4 is added slowly to the hot solution and the mixture is shaken and heated nearly to boiling before filtering, since otherwise the precipitate is likely to pass through the filter.

4. By adding the reagent gradually almost all the barium is precipitated before an excess of K_2CrO_4 is present. This is of importance, since, when much barium is present, even 3 mg. of strontium may be carried down completely if the reagent is added quickly.

5. When less than 1 mg. of barium is present, it is difficult to distinguish the faint turbidity in the colored solution. The mixture is therefore filtered, even when it appears clear; for a very small yellow precipitate can be seen on the filter after washing out the K_2CrO_4 solution.

Procedure 153.—*Confirmation of Barium.*—Pour repeatedly through the filter containing the K_2CrO_4 precipitate (P. 152) a 5–10 cc. portion of hot 6 n. HCl, and evaporate the solution just to dryness. Treat the residue as described in the second paragraph of P. 152, but use only one half as much of each reagent. (Yellow precipitate, presence of BARIUM.)

Notes.—1. In case a large quantity of strontium is present, as shown by the formation of a large precipitate in P. 154, some of it may be precipitated by K_2CrO_4 in P. 152, especially if the directions as to the quantities of the reagents have not been followed. The strontium will not, however, again precipitate in this second treatment; for the quantity of it now present in the solution is much less than before. A yellow precipitate now obtained is therefore conclusive evidence of the presence of barium.

Procedure 154.—*Precipitation of Strontium.*—To the filtrate from the K_2CrO_4 precipitate (P. 152) add 6 n. NH_4OH slowly till the color changes from orange to yellow, and then 5 cc. more. Heat the solution to 60–70°, and add to it 15 cc. of 95% C_2H_5OH 5 cc. at a time, shaking for 10–15 seconds after each addition if a precipitate forms. Cool the solution in running water, shaking it continuously; and let the mixture stand at least 5 minutes. (Light yellow precipitate, presence of STRONTIUM.) In case considerable precipitate forms, add 5 cc. of 3 n. K_2CrO_4 solution and 15 cc. of 95% C_2H_5OH, shake the mixture, and let it stand at least 5 minutes. Filter with the aid of suction (see Note 4); suck the precipitate as dry as possible, but do not wash it.

Treat the precipitate by P. 155. Treat the filtrate by P. 156.

Notes.—1. Under these conditions 1 mg. of strontium yields a precipitate, and 500 mg. of calcium or magnesium do not do so, provided not more than 3 cc. of K_2CrO_4 solution nor more than 15 cc. of C_2H_5OH have been added. Upon the addition of the second portions of these reagents, a precipitate of $CaCrO_4$ may separate when a large quantity of calcium is present. This does not interfere with the detection of strontium; for these additional amounts of reagent are added, in order to precipitate completely a large quantity of strontium, only when the smaller amounts have already produced a considerable precipitate.

2. Since calcium may precipitate even at first if the concentrations of the reagents differ much from those prescribed, the confirmatory test for strontium (in P. 155) should always be tried.

3. The alcohol is added to the hot solution, in small portions, and with vigorous shaking, so that all the $SrCrO_4$ may not be suddenly precipitated, which may cause it to separate in so fine a form that it passes through the pores of the filter-paper.

4. If the filtrate is not perfectly clear, even after a second filtration, it may be made so by adding some paper-pulp, shaking vigorously for a minute or two, and again filtering with the aid of suction. The pulp may be made by shaking violently a filter-paper torn into small pieces with 10 cc. of water in a stoppered test-tube, and pressing out most of the water between the fingers. The precipitate is not washed, since $SrCrO_4$ is fairly soluble in water.

Procedure 155.—*Confirmation of Strontium.*—Pour repeatedly through the filter containing the K_2CrO_4 precipitate (P. 154) a 10-cc. portion of boiling water. Add to the solution just 1 cc. of 3 n. Na_2CO_3 and 12 cc. of 3 n. $K_2C_2O_4$, and boil the mixture gently in a covered casserole for 5 minutes. Filter the boiling mixture. Reject the filtrate. Wash the precipitate thoroughly with water, and pour repeatedly through the filter 5 cc. of cold 1 n. $HC_2H_3O_2$. To the solution add 2 cc. of 1 n. Na_2SO_4, heat the mixture to boiling, and let it stand 10 minutes. (White precipitate, presence of STRONTIUM.)

Notes.—1. By a boiling solution containing oxalate and carbonate in the prescribed proportions small quantities of strontium and calcium are converted in a few minutes almost completely into $SrCO_3$ and CaC_2O_4, respectively. This behavior arises from the facts that in the hot mixture $SrCO_3$ is less soluble than SrC_2O_4, while CaC_2O_4 is less soluble than $CaCO_3$. The mixture is filtered while still near the boiling temperature; for in the cold the solubility relations are such that SrC_2O_4 instead of $SrCO_3$ results.

2. $SrCO_3$ is readily dissolved by 1 n. $HC_2H_3O_2$, but CaC_2O_4 is only slightly dissolved by this acid. Any small quantity of calcium that passes into solution would not give a precipitate with Na_2SO_4, since $CaSO_4$ is a moderately soluble salt. Of any barium that may be contained in the K_2CrO_4 precipitate only enough is dissolved by the boiling water (in the presence of the K_2CrO_4

and NH_4OH remaining in the filter-paper) to give a scarcely noticeable turbidity with the Na_2SO_4 solution.

Procedure 156.—*Separation of Calcium from Magnesium.*—Dilute the ammoniacal filtrate from the K_2CrO_4 precipitate (P. 154) with 50 cc. of water, add just 3 cc. of 3 n. $K_2C_2O_4$, and, unless there is already a precipitate, let the mixture stand at least 15 minutes. (Fine white precipitate, presence of CALCIUM.)

In case there is no precipitate, treat the solution by P. 158.

In case there is a precipitate, heat the mixture nearly to boiling, and add gradually 3–10 cc. more 3 n. $K_2C_2O_4$ solution, adjusting the volume added to the size of the $(NH_4)_2CO_3$ precipitate produced in P. 151. Continue to heat the mixture for 5 minutes; then filter it immediately, and wash the precipitate. Treat the precipitate by P. 157. Treat the filtrate by P. 158.

Notes.—1. Only 3 cc. of 3 n. $K_2C_2O_4$ are added at first, in order to prevent, so far as is possible, the precipitation of MgC_2O_4. This volume of reagent will not precipitate magnesium unless there is present a very large quantity of it (more than 300 mg.), such as would rarely be found (in view of the small equivalent weight of this element) in the one gram of substance taken for analysis. But if a larger volume of the reagent were used, a precipitate might result with a smaller quantity of magnesium.

2. With even this small quantity of the reagent ½ mg. of calcium gives an almost immediate precipitate when not much magnesium is present. But in the presence of a large quantity of magnesium the test is much less delicate; thus, in order to detect 1 mg. of calcium in the presence of 300 mg. of magnesium, the mixture must be allowed to stand for ten to fifteen minutes.

3. To insure the complete precipitation of calcium, a larger volume (3–10 cc.) of the $K_2C_2O_4$ reagent is subsequently added; and, though this may cause the precipitation of some of the magnesium, this is not important since the presence or absence of calcium has already been determined. Enough reagent is added to combine with the magnesium, as well as with the calcium, since the solvent effect of magnesium salt on CaC_2O_4 is thereby diminished. The amount needed is estimated from the size of the original $(NH_4)_2CO_3$ precipitate (in P. 151).

4. The mixture is heated to boiling and the $K_2C_2O_4$ solution is

added slowly, in order to cause the CaC_2O_4 to precipitate in the form of coarser particles that can be more readily filtered. The mixture is kept hot for 5 minutes to insure the complete precipitation of calcium. The mixture is not heated for more than 5 minutes and is filtered immediately, in order to prevent so far as possible the precipitation of $MgC_2O_4 \cdot 2H_2O$. This substance, though slightly soluble in water, has an unusually great tendency to remain in supersaturated solution, especially if agitation of the solution be avoided.

5. Owing to the possibility that the precipitate formed on the first addition of $K_2C_2O_4$ may consist of magnesium or strontium oxalate, the confirmatory test for calcium should not be omitted.

Procedure 157.—*Confirmation of Calcium.*—Treat the $K_2C_2O_4$ precipitate (P. 156), or a small portion of it if it is large, with 5 cc. of 6 n. H_2SO_4 to which 20 drops of C_2H_5OH have been added. To the solution add 10 cc. of 95% C_2H_5OH, and let the mixture stand for several minutes. (White precipitate, presence of CALCIUM.)

Notes.—1. Because of its slight solubility, only a little $CaSO_4$ dissolves in the H_2SO_4; but this is completely thrown out as a flocculent precipitate by the addition to the solution of twice its volume of C_2H_5OH. 1 mg. of calcium produces a turbidity at once, 0.5 mg. in 1–3 minutes, and 0.2 mg. within 10 minutes. This test does not, however, furnish any indication of the quantity of calcium present except when this is very small; for whatever that quantity, not more than about 1 mg. of calcium dissolves in the mixture of 5 cc. of 6 n. H_2SO_4 with 20 drops of C_2H_5OH.

2. The presence of magnesium or of strontium in the $K_2C_2O_4$ precipitate does not interfere with the test. For, even though a moderate quantity of magnesium passed into the H_2SO_4 solution, it would not precipitate on the addition of C_2H_5OH; and the quantity of strontium which dissolves in the H_2SO_4 mixture gives a barely noticeable turbidity when the two volumes of C_2H_5OH are added. A considerable turbidity would result if the amount of strontium dissolved by the H_2SO_4 were not reduced by mixing with it the 20 drops of C_2H_5OH.

Procedure 158.—*Detection of Magnesium.*—To the filtrate from the $K_2C_2O_4$ precipitate (P. 156) add 5 cc. of 15 n. NH_4OH and 25 cc. of 1 n. Na_2HPO_4; cool, and shake the mix-

ture; if no precipitate forms, let the mixture stand for at least half an hour, shaking it frequently. (White precipitate, presence of MAGNESIUM.) Filter.

Wash the precipitate once with 95% C_2H_5OH, and treat it by P. 159.

Notes.—1. $Mg(NH_4)PO_4$ is fairly soluble even in cold water, owing chiefly to hydrolysis. To diminish this hydrolysis the solution is made strongly ammoniacal.

2. In an aqueous solution this substance shows a great tendency to form a supersaturated solution, and it is therefore usually directed to make the test in as small a volume as possible. In the presence of C_2H_5OH, however, precipitation takes place rapidly; and even ½ mg. of magnesium produces a distinct turbidity within half an hour under the conditions of the Procedure. A small precipitate of this kind settles out on further standing, and may then be detected by rotating the solution so as to cause the precipitate to collect in the center.

Procedure 159.—*Confirmation of Magnesium.*—Treat the Na_2HPO_4 precipitate (P. 158), or a small portion of it if it is large, with 5 cc. of 2 n. H_2SO_4; add to the solution 10 cc. of 95% C_2H_5OH, and shake it steadily for two or three minutes. Filter if there is a precipitate; add to the filtrate 10 cc. of water, 20 cc. of 6 n. NH_4OH, and 5 cc. of 1 n. Na_2HPO_4; and let the mixture stand at least half an hour. (White crystalline precipitate, presence of MAGNESIUM.)

Notes.—1. This confirmatory test should be tried whenever Na_2HPO_4 produces a small precipitate that is not distinctly crystalline. For, if even a small quantity of strontium or calcium failed to be precipitated in P. 154 or 156, a flocculent precipitate of $Sr_3(PO_4)_2$ or $Ca_3(PO_4)_2$ would come down on the addition of Na_2HPO_4.

2. The addition of H_2SO_4 and C_2H_5OH precipitates strontium and calcium so completely that any precipitate (more than a very slight turbidity) produced on adding Na_2HPO_4 and NH_4OH to the H_2SO_4 solution cannot be due to these elements.

ANALYSIS OF THE ALKALI GROUP

With Robert H. Dalton and Roger Williams

Tabular Outline XIV

See page 246.

General Discussion

D. 161. Separation into Two Subgroups.—Any scheme for the analysis of this group naturally begins with the separation of the elements into two subgroups, one comprising *sodium* and *lithium,* and the other *potassium, rubidium,* and *cesium.* For this purpose two alternative processes are available—those commonly employed in quantitative analysis for the separation of sodium and potassium—which utilize chloroplatinic acid and perchloric acid, respectively, in alcoholic solution. The suitability of both these processes for the qualitative analysis of this group was studied; and the method with perchloric acid was adopted, mainly because of the greater cheapness of this reagent.

D. 162. Previous Removal of Ammonium Salts and of Sulfate (P. 161).—Ammonium salts are first completely removed by ignition, since otherwise they would pass into both groups and introduce complications. It is also necessary to remove any sulfate that may have been present as a constituent of the original material or has been introduced from the oxidation of the sulfide reagents used in the analysis; for it would cause the precipitation of sodium sulfate with the potassium, rubidium, and cesium perchlorates. Sulfate can be readily removed by adding a salt of barium or of lead. The latter has been here used because of the easy removal of the excess from the solution by means of hydrogen sulfide. An attempt was made to avoid the necessity of removing the sulfate altogether by finding an organic solvent which would dissolve sodium hydrosulfate sufficiently, while at the same time leaving the perchlorates of potassium, rubidium, and cesium substantially undissolved. Formic acid especially was tried, but the perchlorate of potassium was found to be too soluble in it.

Tabular Outline XIV

Analysis of the Alkali Group

Filtrate from $(NH_4)_2CO_3$ precipitate: Na, Li, K, Rb, Cs, as chlorides and perhaps sulfates.
Evaporate, ignite, add water and $Pb(NO_3)_2$, filter (P. 161).

Vapor: NH_4 salts.

Precipitate: $PbSO_4$.

Solution. *Remove lead with H_2S, evaporate with $HClO_4$, add C_2H_5OH (P. 162).*

Filtrate: $NaClO_4$, $LiClO_4$.
Saturate with HCl gas (P. 163).

Precipitate: NaCl.
Add water, $Mg(C_2H_3O_2)_2$, $UO_2(C_2H_3O_2)_2$ (P. 164).

Precipitate, greenish-yellow: $NaMg(UO_2)_3(C_2H_3O_2)_9$.

Filtrate: Li salts.
Evaporate with HNO_3 (caution!), add C_2H_5OH, NH_4OH, and Na_2HPO_4 (P. 165).

Precipitate: Li_3PO_4.

Precipitate: $KClO_4$, $RbClO_4$, $CsClO_4$.
Treat with $Na_3Co(NO_2)_6$ (P. 166).

Precipitate: K, Rb, Cs as cobaltinitrite.
Add 9 n. $NaNO_2$, evaporate, ignite, add water (P. 166).

Residue, black: CoO and Co_3O_4.

Filtrate: KNO_2, $RbNO_2$, $CsNO_2$.
Add $HC_2H_3O_2$ and $Bi(NO_3)_3$ (P. 167).

Filtrate: KNO_2, $(NaNO_2)$.
Add $Co(NO_3)_2$ (P. 168).

Precipitate, yellow: $K_2NaCo(NO_2)_6$.

Precipitate, yellow: $Rb_2NaBi(NO_2)_6$, $Cs_2NaBi(NO_2)_6$.
Dissolve in HCl, add $SbCl_3$ (P. 169).

Precipitate: *3CsCl.2SbCl$_3$.

Filtrate: RbCl, †CsCl, ($BiCl_3$, $SbCl_3$).
Pass in H_2S (P. 170).

Filtrate: RbCl, CsCl.
Evaporate, add NaHTart.

Precipitate: RbHTart.
Confirm by P. 171.

Filtrate: CsCl.
Add silicotungstic acid (P. 172).

Precipitate: Cs silicotungstate.

Precipitate: Bi_2S_3, Sb_2S_3.

*† For the significance of these signs see page 9.

D. 163. The Perchlorate Separation (P. 162).—By determining the most suitable quantities and proportion of concentrated perchloric acid and of 99% ethyl alcohol it was found possible to get a precipitate with less than 1 mg. of potassium, rubidium, or cesium, and retain in solution 500 mg. of sodium or 200 mg. of lithium.

An extended study of the perchlorates of the elements of this group in various organic solvents has been made by Willard and Smith.[1] The fact that they found that the perchlorates of the two subgroups show greater differences in solubility in ethyl acetate or in mixtures of it with ethyl alcohol than in ethyl alcohol alone led to an investigation of the relative advantages of these two solvents. It was found, however, in the presence of perchloric acid, that the volume of ethyl acetate required for dissolving 500 mg. of sodium prevents the precipitation of 1 mg. of cesium.

D. 164. Separation and Detection of Sodium and Lithium (P. 163–165).—These elements are separated by saturating the alcoholic solution with hydrogen chloride gas. The separation is entirely satisfactory, in that 1 mg. of sodium gives a precipitate, and 0.3 mg. of lithium is detectable in the filtrate when 500 mg. of sodium are also present; and a simpler method can hardly be found, considering that the elements are already present in strong alcoholic solution.

The formation of a precipitate with hydrogen chloride is, to be sure, not highly characteristic of sodium. Its presence in any precipitate produced must therefore be confirmed. For this purpose it has been found that the reagent magnesium uranyl acetate, proposed by Blanchetière,[2] is far more satisfactory than the commonly employed potassium pyroantimonate. The former reagent was therefore adopted. With it 0.5 mg. of sodium yields a voluminous precipitate, and other elements of the alkali group or alkaline-earth group give no precipitate, at any rate when present in small quantity (such as 10 mg. or in case of lithium not more than 5 mg.). Moreover, there is no difficulty in securing good blank tests, while with the pyroantimonate amorphous precipitates not due to sodium often result.

[1] Willard and Smith, *J. Am. Chem. Soc.*, **45**, 293 (1923); Smith, *ibid.*, **47**, 765, 768 (1925).

[2] Blanchetière, *Bull. soc. chim.*, (4), **33**, 807–818 (1923).

The sensitive reaction for sodium described by Ball[1] was also studied. This consists in precipitating the sodium as a triple nitrite by a reagent containing potassium, cesium, and bismuth nitrites. The process was not employed mainly because of the expense and instability of the reagent. Moreover, a very delicate test for sodium has no advantage, since a small quantity of it is likely to be introduced in the course of the analysis from the reagents and vessels employed.

The detection of lithium in the alcoholic filtrate is somewhat less simple, since the solution contains also much perchloric acid and hydrochloric acid, largely ionized acids, which prevent the precipitation of slightly soluble lithium salts of weak acids, such as the phosphate or fluoride. Moreover, evaporation and fuming to remove these acids cannot be directly carried out owing to the violent explosions that result from the presence of ethyl perchlorate. A process of evaporation for avoiding such explosions was, however, worked out; and the best conditions for the phosphate precipitation were determined so that 0.1–0.2 mg. of lithium could be detected, which is desirable because of its very small equivalent weight. Precipitation from a strongly ammoniacal alcohol-containing solution (rather than from sodium hydroxide solution as usually employed) was found to give the best results.

D. 165. Conversion of the Perchlorates of Potassium, Rubidium, and Cesium into Soluble Salts (P. 166).—The first step in the detection of potassium, rubidium, and cesium must be the transformation of their perchlorates into readily soluble salts. The method of doing this which, in principle at any rate, would seem simplest is to convert the perchlorates into chlorides by ignition. The temperature required for complete conversion, however, is so high that, if the ignition be carried out in a crucible or dish, even though it be kept covered, there is likely to be complete loss of a small quantity of the alkali elements through volatilization of their chlorides. Moreover, with larger quantities bad frothing results which carries part of the material into the upper part of the crucible, where it is difficult to subject it to sufficiently strong ignition. Attempts were made to improve the conditions by mixing with the perchlorates oxalic acid or manganese dioxide;

[1] Ball, *J. Chem. Soc, London*, 95, 2128 (1909).

but the conversion was still not complete. It was finally found that a fairly satisfactory result was secured by carrying out the ignition in a wide pyrex-glass tube of such length that most of the volatilized material condensed on the upper parts of the tube.

Unfortunately, however, even the chlorides are not suitable for the process which is to be employed for the separation of potassium from rubidium and cesium (involving the use of sodium and bismuth nitrites), both because potassium chloride is not soluble enough in water to yield the highly concentrated solution needed, and because chloride precipitates the bismuth as oxychloride. As it is particularly advantageous for that separation to have the elements in the form of nitrites, it seemed most natural to convert the chlorides into nitrites, which can be done by shaking the solution with solid silver nitrite, filtering off the precipitated silver chloride and excess of silver nitrite, removing the small quantity of silver still present with hydrogen sulfide, and evaporating the filtrate.

This process was used in the earlier analyses; but it is a time-consuming one, and without special care the conversion of a large quantity of perchlorate to chloride by ignition may be incomplete. It is therefore fortunate that a much simpler method was discovered by Mr. R. H. Dalton. This consists, first, in converting the perchlorates into the less soluble cobaltinitrites by digestion with excess of sodium cobaltinitrite; and second, in decomposing the precipitated cobaltinitrites into the simple alkali nitrites and cobalt oxide by adding a little strong sodium nitrite solution, evaporating, and igniting. It was found that this second decomposition is readily made complete merely by igniting the evaporated mixture in a small casserole at a low temperature.

D. 166. Separation of Rubidium and Cesium from Potassium (*P. 167*).—Apparently by far the best process available for separating rubidium and cesium from potassium is that based on the discovery of W. C. Ball[1] that the first two elements form very slightly soluble triple nitrites with sodium and bismuth, such as $Rb_2NaBi(NO_2)_6$, while the potassium salt is so very soluble that it can be produced only at exceptional concentrations of the components. Certain difficulties had to be overcome in adapting this separation to the present purpose in order to realize conditions

[1] Ball, *J. Chem. Soc. London*, 95, 2127 (1909).

under which the minimum quantity of rubidium could be precipitated, and under which the bismuth reagent would not of itself give a precipitate on mixing or standing with sodium nitrite solution. It was found practicable to overcome these difficulties to such an extent that 1 mg. of rubidium in the presence of 100 mg. of potassium, or 2 mg. in the presence of 500 mg. of potassium could be detected.

This process as a whole has the advantage, especially important in rare-element qualitative analysis, that in the common case where the rare elements are not present the absence of all of them (of rubidium and cesium in this case) is once for all determined, making it necessary to test further only for the common elements (potassium in this case).

D. 167. Detection of Potassium (*P. 168*).—This method has the further simplification that potassium can be detected in the filtrate from the rubidium and cesium precipitate merely by adding cobalt nitrate to the solution, since the large concentration of sodium nitrite there prevailing is especially favorable for the precipitation of potassium as cobaltinitrite.

There is involved, to be sure, the complication that rubidium cobaltinitrite is much less soluble than the potassium salt and than the rubidium precipitate produced by sodium bismuthinitrite. But this difficulty was overcome by a device, which may be useful in other similar cases; namely, by adding at first only such a minute quantity of cobalt reagent as suffices to precipitate and remove the 0.5–1.0 mg. of rubidium that may be present, but not to precipitate a significant proportion of the potassium.

D. 168. Separation and Detection of Rubidium and Cesium (*P. 169–172*).—For the separation of rubidium and cesium four reagents deserve especial consideration. Two of these, sodium hydrotartrate and sodium 6-chloro-5-nitrotoluenemetasulfonate, give less soluble precipitates with rubidium; and two of them, antimony trichloride and silicotungstic acid, form less soluble compounds with cesium. But with none of them is the difference in the behavior of the rubidium and cesium salts sufficient to enable 1 mg. of either element to be separated from 100 mg. of the others in a single operation. This result was attained, however, by employing the reagents in succession.

The process adopted consists essentially of the following steps. First, to a solution of the chlorides in a suitable small volume of 6 normal hydrochloric acid antimony trichloride is added, whereby any cesium in excess of about 5 mg. is precipitated and all the rubidium (at any rate up to 100 mg.) is left in solution. Second, to the filtrate, after removing the antimony with hydrogen sulfide and evaporating off the acid, a small volume of saturated solution of sodium hydrotartrate or of sodium chloronitrotoluenemetasulfonate is added, whereby there is precipitated all the rubidium but none of the small quantity of cesium that may be present. Third, to the filtrate silicotungstic acid is added, whereby the cesium is precipitated. This process was found to be satisfactory for the detection of 1 mg. of either element in the presence of 100 mg. of the other. Neither the cesium precipitate with antimony trichloride nor the rubidium precipitate with hydrotartrate carries down the other element to an important extent. The result was not satisfactory in this respect, however, when the attempt was made to dispense with the antimony trichloride and precipitate the cesium with silicotungstic acid in the presence of a small quantity of rubidium, such as remains in solution when this element is precipitated by hydrotartrate from a volume of solution large enough to keep 100 mg. of cesium in solution; for all of a little rubidium was carried down in the cesium precipitate.

The chloronitrotoluenemetasulfonate, whose different behavior towards the various alkali elements was observed by Davies,[1] is more satisfactory than the hydrotartrate for detecting a small quantity of rubidium; but, since the reagent may not be available, the hydrotartrate is employed in the regular procedure.

[1] Davies, *J. Chem. Soc. London*, **123**, 2976 (1923).

MODIFICATIONS OF THE PROCESS INVESTIGATED

D. 169. Separation of Potassium from Rubidium and Cesium by Chloroplumbic Acid.—Before the bismuthinitrite method became available, a separation of these elements was worked out [1] on the basis of the facts discovered by Wells [2] that the salts of chloroplumbic acid (H_2PbCl_6) with rubidium and cesium are much less soluble than that of potassium. The procedure consisted in treating the dry chlorides, such as would result from ignition of the perchlorates, with 4 cc. of cold 12 n. HCl, decanting from any undissolved salt (consisting of potassium chloride) the solution, which would contain all the rubidium and cesium (even up to 500 mg.) but not more than 50 mg. of potassium, adding to it over half its volume of chloroplumbic reagent, and saturating the mixture with chlorine gas (the chloroplumbic reagent being prepared by passing chlorine gas into 12 normal hydrochloric acid in contact with a large excess of solid lead chloride, till the mixture even after standing is completely saturated with chlorine). Under these conditions the maximum quantity of potassium that passes into the hydrochloric acid solution gives no precipitate with chloroplumbic reagent, and 1–2 mg. of rubidium or 1 mg. of cesium, if present in that solution, yields a precipitate. To what extent small quantities of the latter elements pass into the acid solution when present with a large quantity (500 mg.) of potassium was not conclusively determined; but 2 mg. of rubidium were in one experiment retained by the precipitate of potassium chloride almost completely. The method may, therefore, be used for the qualitative separation of rubidium and cesium from moderate quantities of potassium (such as 50 mg.), but cannot be safely employed, pending further investigation, for their separation from larger quantities of potassium.

D. 170. Another Method of Separation of Potassium, Rubidium, and Cesium.—Since this System of Analysis was given to the publisher, there has been described by Ato and Wada [3] a new method for the analysis of the alkali group, which has been investigated in the systematic way here followed, and is sup-

[1] By J. E. Ober and Roger Williams.

[2] Wells, *Am. J. Sci.* (3), 46, 184–187 (1893).

[3] Ato and Wada, *Sci. Papers Inst. Phys. Chem. Research*, 4, 261–293 (1926).

ported by a wealth of confirmatory experiments. It employs, like the process here adopted, perchloric acid and alcohol for the separation of sodium and lithium from the other elements, and hydrogen chloride gas for that of sodium and lithium from each other. The method used for separating potassium, rubidium, and cesium differs, however, greatly from that here adopted; though it involves some of the operations earlier employed by Ober and Williams, before the more perfect separations with bismuthinitrite and silicotungstic acid became available. It consists largely in an ingenious combination of processes of fractionation by which the elements are finally fully separated; thus it includes the treatments with concentrated hydrochloric acid and with antimony trichloride described in D. 169 and 168; and utilizes the different solubilities of rubidium and cesium carbonates in ethyl alcohol. In consequence, the process is more lengthy than the one here presented.

ANALYSIS OF THE ALKALI GROUP

Tabular Outline XIV

See page 246.

Procedures and Notes

Procedure 161.—*Removal of Ammonium Salts and of Sulfate.*—Evaporate the $(NH_4)_2CO_3$ filtrate (P. 151) to dryness in a casserole. Ignite the residue over a flame below a red heat till fumes of ammonium salts no longer escape, keeping the dish in motion and heating the sides as well as the bottom of the dish. Cool the casserole, add 5 cc. of water and one drop of 6 n. NH_4OH, filter out and reject any residue, using a very small filter, evaporate the solution, preferably in a 20-cc. pyrex bowl, and ignite the residue as before. (Residue, presence of ALKALI GROUP.) (See Note 3.) Cool the bowl, add 1–3 cc. of 16 n. HNO_3, evaporate, and gently ignite the residue. After cooling, add 5–10 cc. of water, then 1 n. $Pb(NO_3)_2$, 0.1 cc. at a time, till there is no further precipitate, shake the mixture, and let it stand 5 minutes. Filter out and reject the precipitate. Saturate the filtrate with H_2S, and filter it.

Treat the filtrate by P. 162. Reject the precipitate.

Notes.—1. Before analyzing for the alkali group, the ammonium salts are removed by ignition, since in the treatment with $HClO_4$ and ethyl alcohol they would pass both into the precipitate and into the filtrate, and then give precipitates in the subsequent tests. Care must therefore be taken to volatilize it completely by heating all parts of the residue. The dissolving of the residue in a little water and the following evaporation and ignition help to ensure its complete removal. In the ignition the residue is not heated to a red heat, since at that temperature alkali chlorides are somewhat volatile.

2. A brown or black residue of organic matter, coming from impurity in the ammonium salts added in the course of analysis and from the alcohol and filter paper, may remain upon treating the ignited residue with water. There may also be a white residue of silica, arising from the action of the reagents on the glass and porcelain vessels throughout the course of the analysis.

Moreover, a flocculent precipitate of $Al(OH)_3$ or other hydroxide may form on adding NH_4OH. Any such residue is filtered out and the solution is evaporated before deciding as to the presence or absence of the alkali group. A glass bowl, rather than a casserole, is used to permit a better estimate of the amount of residue.

3. A small residue of alkali element coming from impurities in the reagents and action on the vessels may also result; but this is likely to contain less than 0.5 mg. of sodium or potassium, provided in the preparation of the solution and the isolation of the preceding groups the purest reagents on the market and only pyrex glass and porcelain vessels have been employed. Since, however, there is often a slight residue of alkali element, and since on the other hand in the dry form even a residue that appears negligible may contain an appreciable quantity of an alkali element, it is advisable in a doubtful case to determine whether the amount present is really significant, either by comparing the residue with that resulting on evaporating a solution of 0.5 mg. of sodium as NaCl or by weighing the bowl accurately after the second ignition, dissolving and washing out the residue, and igniting, cooling, and weighing the empty bowl.

4. Sulfate must be removed when more than a few milligrams are present, since it would cause sodium to precipitate as Na_2SO_4 or $NaHSO_4$ with the potassium, rubidium, and cesium perchlorates upon treating with $HClO_4$ and C_2H_5OH. It can be completely eliminated by the addition to a nearly neutral solution of either a soluble barium or lead salt. $Pb(NO_3)_2$ is used, since the excess of lead can be removed merely by saturating with H_2S gas and filtering. The residue is heated with HNO_3 before adding the $Pb(NO_3)_2$, so as to displace the chloride-ion by nitrate-ion and thus avoid precipitation of $PbCl_2$.

Procedure 162.—*Separation of Sodium and Lithium from Potassium, Rubidium, and Cesium.*—To the filtrate * from the H_2S precipitate (P. 161) in a 25-cc. casserole add 1–5 cc. of 9 n. $HClO_4$, according to the amount of residue obtained in P. 161, and evaporate cautiously till the $HClO_4$ fumes strongly. Let the mixture cool completely, rinse it into a dry flask with four times as much 99% C_2H_5OH as was added of 9 n. $HClO_4$, stopper the flask, cool it, and let it stand for 15 minutes with

* For practice-analyses use a mixture of test-solutions (1 cc. of each) of sodium, lithium, potassium, rubidium, and cesium.

occasional shaking. (Precipitate, presence of POTASSIUM, RUBIDIUM, or CESIUM.) Filter the mixture through a small dry filter, collecting the filtrate in a small dry flask, and wash the precipitate with 2 cc. of 99% C_2H_5OH.

Analyze the filtrate by P. 163–165 for sodium and lithium.

Analyze the precipitate by P. 166–172 for potassium, rubidium, and cesium; first uniting with it any precipitate obtained on cooling the $HClO_4$ solution in P. 6.

Notes.—1. Enough $HClO_4$ must be added to convert into perchlorates the nitrates of the sodium and lithium, as well as of the potassium, rubidium, and cesium, since otherwise sodium and lithium may be precipitated (as nitrates) on the subsequent addition of C_2H_5OH. For 500 mg. of sodium or 150 mg. of lithium about 2.5 cc. of 9 n. $HClO_4$ are theoretically required. In addition, a moderate excess is desirable to give fluidity to the mixture during the fuming. The quantity of 9 n. $HClO_4$ added is varied between 1 cc. and 5 cc. according to the amount of alkali elements present, since an undue excess increases the solubility of the precipitates. To displace the nitric acid completely, the mixture must be heated till the $HClO_4$ fumes strongly.

2. About 20 cc. of 99% C_2H_5OH are required for the complete solution of 500 mg. of sodium as perchlorate when 5 cc. of 9 n. $HClO_4$ have been added; and in this mixture more than 200 mg. of lithium dissolves. Even when 1–2 mg. of sodium or 0.3 mg. of lithium is present with 500 mg. of potassium, a sodium precipitate results with HCl in P. 163, and the final tests for sodium and lithium are obtained in P. 164 and 165.

3. From 3 cc. of 9 n. $HClO_4$ and 20 cc. of 99% C_2H_5OH even 1 mg. of potassium, rubidium, or cesium gives almost immediately a finely crystalline precipitate. The precipitation is more complete when the C_2H_5OH added is 99% instead of more dilute, and when the volume added is two to four times that of the 9 n. $HClO_4$, instead of larger or smaller than this. To avoid dilution of the alcohol care is taken to use dry apparatus and a dry filter. Even 0.5 mg. of cesium, the element most difficult to detect, gives a distinct precipitate with 1 cc. of 9 n. $HClO_4$ and 4 cc. of 99% C_2H_5OH. To ensure more complete separation the mixture is cooled and allowed to stand about 15 minutes with occasional shaking. Under these conditions 500 mg. of potassium in 5 cc. of 9 n. $HClO_4$ and 20 cc. of 99% C_2H_5OH are so completely re-

moved that no precipitate forms with HCl in P. 163 or with Na_2HPO_4 in P. 165.

4. The precipitate is washed with only a little C_2H_5OH, since thorough washing is unnecessary. By 2 cc. of 99% alcohol less than 0.1 mg. of potassium, rubidium, and cesium is dissolved.

5. With the precipitate is united any salt that separated on cooling the $HClO_4$ solution in P. 6, since the latter may not consist only of $KClO_4$, but may have carried down all of a small quantity of rubidium or cesium. Thus at least 2 mg. of rubidium are precipitated at that point with 500 mg. of potassium.

Procedure 163.—*Separation of Sodium from Lithium.*—Saturate the C_2H_5OH solution (P. 162) with HCl in a flask fitted with a two-hole cork stopper and surrounded with cold water by passing through it a rapid current of the dry gas (see Note 4) till HCl fumes escape from the flask; and let the solution stand half an hour. (Precipitate, presence of SODIUM.) Filter the mixture through a dry 3–5 cm. filter-paper. Wash the precipitate thoroughly with not more than 5 cc. of 99% C_2H_5OH saturated with dry HCl gas. Add at once to the filtrate one fourth its volume of water.

Treat the precipitate by P. 164.

Treat the filtrate by P. 165 (*under no circumstances heating it otherwise than as there directed*).

Notes.—1. Under the conditions of the Procedure 0.5 mg. of sodium gives a precipitate, and 100 mg. of lithium do not do so. Furthermore, lithium can be detected in the filtrate when only 0.3 mg. of it is present with 500 mg. of sodium.

2. The precipitation of the sodium will be incomplete if the alcohol is not completely saturated with HCl, or if water has been introduced in P. 162 or by using moist HCl gas in this Procedure.

3. The filter is washed thoroughly with C_2H_5OH to remove any lithium present in the adhering liquid, since this might give a precipitate in the confirmatory test for sodium in P. 164. A minimum quantity of 99% C_2H_5OH saturated with HCl is used, so as to avoid dissolving the NaCl. The filtrate is diluted at once with a little water, so as to decompose in the subsequent evaporation (in P. 165) some of the $C_2H_5ClO_4$ which has been found, and thus lessen the danger of explosion.

4. The following is a convenient method of generating the dry HCl gas. Put 100 g. of coarse NaCl into a 500-cc. conical pyrex

flask fitted with a two-hole rubber stopper carrying a small-bore delivery tube leading into the alcoholic solution and carrying a thistle-tube whose stem ends just below the top of a short test-tube filled with 95% H_2SO_4 and resting on the bottom of the flask. Pour through the thistle-tube 95% H_2SO_4, 5–10 cc. at a time, as often as is needed to produce a vigorous action, until 100 cc. have been added. Thereafter warm the mixture on an electric hot plate enough to cause the rapid evolution of gas to continue (but not heating it above 80°). After the alcoholic solution is saturated, check the flow of gas by immersing the flask in cold water, and set aside the generator for use on a later occasion. Since the HCl is at first eagerly absorbed by the alcohol, it is essential, in order to avoid sucking back into the generator, that the thistle-tube function properly as a safety tube, which it does best when arranged as just described. The heating should be so regulated as to secure a rapid flow of gas, both to diminish the tendency to suck back and to lessen the time required for the saturation. The use of strong H_2SO_4 in this generator obviates the need of drying the gas.

Procedure 164.—*Confirmation of Sodium.*—Pour repeatedly through the filter containing the HCl precipitate (P. 163) a 5-cc. portion of water. To the solution add 1 cc. of 95% C_2H_5OH and 5 cc. of magnesium uranyl acetate reagent. (Dense greenish-yellow precipitate, presence of SODIUM.)

Treat the mixture no further.

Notes.—1. Even ½ mg. of sodium yields a relatively large precipitate almost immediately. 10 mg. of potassium, rubidium, cesium, or calcium give no precipitate even on standing over night. 2 mg. of lithium also give no precipitate, but with 5–10 mg. a precipitate forms after a few minutes and then gradually increases. The addition of C_2H_5OH causes the sodium precipitate to separate more rapidly and completely. Its composition corresponds to the formula $NaMg(UO_2)_3(C_2H_3O_2)_9 \cdot 9H_2O$. It separates as small greenish-yellow crystals.

2. The magnesium uranyl acetate reagent is 0.5 n. in uranyl acetate, 3 n. in magnesium acetate, and 2 n. in acetic acid.

3. When only little sodium is present, the quantity of it can be best estimated from the appearance of this precipitate. But, when much is present, its quantity should be estimated from the size of the HCl precipitate in P. 163; for the 5 cc. of reagent added are equivalent to only 9 mg. of sodium.

Procedure 165.—*Detection of Lithium.*—Evaporate the C_2H_5OH-HCl solution (P. 163) in a casserole on a *steam-bath* until the volume becomes that of the 9 n. $HClO_4$ added in P. 162. Cool the mixture to room temperature, add *cautiously* 16 n. HNO_3, a drop or two at a time, as long as action occurs, then 1 cc. more, and heat it on a steam-bath (*not over a flame*) for 10–15 minutes. Then add 0.5 cc. more 16 n. HNO_3, heat the casserole on a wire gauze over a flame until all the $HClO_4$ is expelled, and ignite the residue for a minute or two at a temperature below redness. (*Do not on any account heat the mixture to fuming before the treatment with HNO_3;* and, even after that treatment, *carry out the heating so that, should an explosion occur, it could do no harm.*) Cool the casserole, add to it 3 cc. of 95% C_2H_5OH and two drops of 15 n. NH_4OH, and filter out and reject any residue, using a 3-cm. filter-paper. To the solution in a test-tube add 3 cc. of 15 n. NH_4OH, warm it to 35–40°, add to it two drops of 0.5 n. Na_2HPO_4, and shake it thoroughly to dissolve any local precipitate of Na_2HPO_4. (Precipitate, presence of LITHIUM.) If a precipitate results, add 2 cc. of water, and continue to add 0.5 n. Na_2HPO_4, 1 cc. at a time, as long as it produces a precipitate.

Treat the mixture no further.

Notes.—1. The alcoholic solution is first evaporated on a steam-bath to expel the C_2H_5OH and HCl. The residual liquid is then heated with 16 n. HNO_3 on a steam-bath to ensure the complete destruction of any remaining C_2H_5OH and of the very explosive $C_2H_5ClO_4$ (ethyl perchlorate) that is formed by combination of C_2H_5OH and $HClO_4$ under the strongly dehydrating conditions prevailing in P. 163. It is essential that these organic substances be destroyed before the mixture is heated above 100°, since there may otherwise result an explosion violent enough to blow the dish to pieces. After proper treatment with HNO_3 an explosion will not result; but, as a precaution, the evaporation over a flame should be carried out in such a manner that an explosion could not injure anyone.—In the first evaporation on a steam-bath an explosion will not occur provided the alcoholic solution was previously diluted with a little water as directed in P. 163.

2. The HNO_3 is added cautiously to the cold mixture, since otherwise it may cause a violent gas evolution, accompanied even by flame if added to the hot mixture. The residue is heated over a flame to ensure the complete removal of the $HClO_4$, since otherwise NH_4ClO_4 might precipitate in the subsequent test. The temperature is kept below a red heat to avoid volatilizing LiCl.

3. The 3 cc. of 95% C_2H_5OH added suffice to dissolve 100 mg. of lithium as LiCl. The two drops of 15 n. NH_4OH added precipitate elements of preceding groups which might be present and give a precipitate with the Na_2HPO_4.

4. The solution tested with Na_2HPO_4 is made to consist of equal volumes of 95% C_2H_5OH and 15 n. NH_4OH, since the solubility of Li_3PO_4 in water is greatly reduced both by C_2H_5OH and by NH_4OH (owing partly to diminished hydrolysis in the latter case). A larger proportion of alcohol is not used, in order to avoid the precipitation of $Na_2NH_4PO_4$; and the solution is warmed for the same reason. Only two drops of 0.5 n. Na_2HPO_4 are added at first so as to avoid introducing much water into the solution and so as to promote the precipitation of a small quantity of Li_3PO_4. Under these conditions even 0.1 mg. of lithium gives a precipitate almost immediately. This delicacy of the test is desirable, because of the very small equivalent weight of this element. To estimate the quantity present more 0.5 n. Na_2HPO_4 is finally added; the mixture being first treated with 2 cc. of water and this somewhat dilute reagent being used so as to avoid precipitation of $Na_2NH_4PO_4$ by the C_2H_5OH and NH_4OH present.

Procedure 166.—*Conversion of the Precipitated Perchlorates into Nitrites.*—Transfer the $HClO_4$ precipitates (P. 162) to a casserole with the aid of a little boiling water. Evaporate off the water; and add to the residue 3–12 cc. of a mixture of 1 f. $Na_3Co(NO_2)_6$ reagent with one half its volume of 6 n. $HC_2H_3O_2$; this mixture having been previously saturated with powdered $NaNO_2$, let stand 10–15 minutes, and freed from any precipitate by filtration. Stir the mixture frequently for 10–15 minutes. (Precipitate, presence of POTASSIUM, RUBIDIUM, or CESIUM.) Filter off the precipitate, and wash it with 5–10 cc. of 1 f. $Na_3Co(NO_2)_6$ reagent diluted with ten volumes of water. Reject the filtrate. Transfer the precipitate to a 25-cc. casserole, add 1 cc. of potassium-free 9 n. $NaNO_2$,

evaporate the mixture to dryness, and ignite the residue gently till it fuses and effervescence ceases. Cool the casserole, add 5–10 cc. of water, and filter the mixture. Reject the black residue. Evaporate the solution just to dryness. Add just 1 cc., or 2 cc., of water (according as the $HClO_4$ precipitate was not, or was, so large that some of it separated in P. 6); then add 6 n. $HC_2H_3O_2$, one drop at a time, till the mixture does not turn red litmus-paper blue. Filter it, if there is any precipitate or residue, through a very small filter. Collect the solution in a small test-tube.

Treat this nitrite solution by P. 167.

Notes.—1. For the subsequent separation of potassium from rubidium and cesium (in P. 167) these elements must be in the form of readily soluble salts, preferably of their nitrites. To obtain them in this form the slightly soluble perchlorates are first converted by metathesis into the still less soluble cobaltinitrites through treatment with excess of $Na_3Co(NO_2)_6$; and the cobaltinitrites are then decomposed into cobalt oxides and the simple nitrites by gentle ignition with an excess of $NaNO_2$.

2. Even 500 mg. of potassium as $KClO_4$, when finely divided, are completely metathesized by excess of $Na_3Co(NO_2)_6$ in 15–20 minutes.

3. Since a large quantity of $NaNO_2$ is added and the best commercial product is seldom entirely free from potassium, $NaNO_2$, $Co(NO_3)_2$, and $HC_2H_3O_2$ are not added separately to the solution to be analyzed, but the $Na_3Co(NO)_6$ reagent is prepared in advance by mixing these substances with one another, so that any potassium may be precipitated and removed by filtration. Moreover, the 1 cc. of 9 n. $NaNO_2$ added just before the ignition must be a reagent that has been freed from potassium, best as described in the Appendix on Reagents.

4. To the dry residue of alkali-element nitrites finally obtained only 1 cc. or 2 cc. of water is added, since the solution must be of small volume and highly concentrated in $NaNO_2$ in order to ensure the precipitation of a small quantity of rubidium by the bismuth nitrate reagent in P. 167. Only 1 cc. of water is used whenever the residue does not contain a large quantity of the alkali elements; but 2 cc. have to be used when much potassium is present, since otherwise it would precipitate with the bismuth reagent. The solution is finally neutralized with a little $HC_2H_3O_2$,

since nitrite solutions become alkaline on evaporation and ignition, and this would later cause precipitation of basic bismuth salt.

Procedure 167.—*Separation of Rubidium and Cesium from Potassium.*—To the nitrite solution (P. 166) in a small test-tube add one sixth its volume of $Bi(NO_3)_3$ reagent, shake the mixture till any local precipitate redissolves, stopper the test-tube, and let it stand 15–30 minutes in a mixture of ice and water. Then warm it to 30°, and stir it frequently for 5 minutes or longer if there is a coarsely crystalline precipitate which seems to be dissolving. (Yellow crystalline precipitate, presence of RUBIDIUM or CESIUM.) If a large precipitate has separated, add 0.5 cc. more $Bi(NO_3)_3$ reagent and 0.5 cc. of 9 n. $NaNO_2$, and let the mixture stand 30 minutes in ice and water; then warm it to room temperature, stirring frequently. Filter the mixture through a small dry filter, and wash the precipitate carefully with not more than 2 cc. of an ice-cold mixture of 10 n. $NaNO_2$ with one fourth its volume of $Bi(NO_3)_3$ reagent.

Treat the filtrate by P. 168. Treat the precipitate by P. 169.

Notes.—1. This separation depends on the facts that rubidium and cesium react with $NaNO_2$ and $Bi(NO_3)_3$ to form slightly soluble salts of the composition $Rb_2NaBi(NO_2)_6$ and $Cs_2NaBi(NO_2)_6$, while the corresponding salt of potassium is readily soluble (as are also those of ammonium, lithium, and of alkaline-earth elements).

2. To make as complete as possible the precipitation of the cesium salt, and especially of the more soluble rubidium salt, the solution should be of small volume, highly concentrated in $NaNO_2$ but only moderately so in bismuth, and it should be kept at 0° for 15 minutes or more. Moreover, the hydrogen-ion concentration should not be much larger than that which arises from $HC_2H_3O_2$. These conditions are secured by preparing the solution to be tested in the way directed in P. 166, and by using as the bismuth reagent a saturated solution of $Bi(NO_3)_3 \cdot 5H_2O$ in 6 n. $HC_2H_3O_2$ (which is approximately 4 n. in bismuth).

3. In order to prevent the precipitation of bismuth by hydrolysis, it is necessary that there be a fair proportion of $HC_2H_3O_2$ in the solution. Prolonged contact with air causes gradual precipitation of a bismuth compound: this may be avoided by displacing

the air from the tube in which the test is made with CO_2 or illuminating gas. When the $Bi(NO_3)_3$ reagent is being added a local precipitate may appear, but this dissolves rapidly on shaking.

4. Under the prescribed conditions, when the nitrite residue is dissolved in 2 cc. of water, 500 mg. of potassium give no precipitate; and 1 mg. of rubidium, even when present with 500 mg. of potassium, yields a precipitate after 5 minutes' standing in ice and water. Moreover, a precipitate results with 0.5 mg. of rubidium or cesium when present alone, provided the residue is dissolved in only 1 cc. of water. It is important, however, to increase the water added to the residue from 1 cc. to 2 cc. when a large amount of potassium is present, since with the smaller volume some of this element may precipitate. Furthermore, 100 mg. of rubidium or cesium are precipitated so completely (after the additional 0.5 cc. of $Bi(NO_3)_3$ reagent and 0.5 cc. of 9 n. $NaNO_2$ have been added) that not more than 1 mg. remains in the solution; and none of a small quantity of potassium is carried down with these elements.

Procedure 168.—*Detection of Potassium.*—To the filtrate from the bismuthinitrite precipitate (P. 167) add from a dropper one drop of 0.3 n. $Co(NO_3)_2$, warm it in a vessel of water to 35° for 10 minutes, cool it in ice and water, keep it there for one hour, and filter out and reject the precipitate. To the filtrate add 0.5 cc. of 6 n. $HC_2H_3O_2$, 2 cc. of water, and 0.2–2.0 cc. of 3 n. $Co(NO_3)_2$, and let the mixture stand at least 30 minutes. (Yellow precipitate, presence of POTASSIUM.)

Treat the mixture no further.

Notes.—1. A small quantity (0.5–1.0 mg.) of rubidium always escapes precipitation by the $Bi(NO_3)$ reagent in P. 167. This gives a precipitate on the addition of $Co(NO_3)_2$; and, in order to decide as to the presence of potassium, it is first removed by the addition of one drop of 0.3 n. $Co(NO_3)_2$. This contains about 0.01 milliequivalent of cobalt, which is theoretically capable of combining with 1.7 mg. of rubidium or 0.8 mg. of potassium to form $Rb_2NaCo(NO_2)_6$ or $K_2NaCo(NO_2)_6$. When the solution is warmed and subsequently kept at 0° for an hour or more, the residual rubidium is in fact so completely precipitated that it gives no precipitate on adding to the somewhat diluted filtrate the larger quantity of $Co(NO_3)_2$. Any precipitate thus obtained from the filtrate therefore shows the presence of potassium.

2. When even 1 mg. of potassium is present, like rubidium it gives a precipitate with the first drop of $Co(NO_3)_2$; but enough of it passes into the filtrate to give a precipitate on standing with the excess of this reagent. When a larger quantity of potassium is present, the first precipitate contains only a negligible proportion of it.

Procedure 169.—*Partial Separation of Cesium from Rubidium.*—Dissolve the bismuthinitrite precipitate (P. 167) in 3 cc. of 6 n. HCl, by placing the opened filter in the mouth of a test-tube and pouring the acid over it. Boil the solution a few moments till the nitrogen oxides are expelled. Cool the solution, add to it 10 drops of 6 f. $SbCl_3$ reagent, and let it stand 30 minutes with frequent stirring. (White crystalline precipitate, presence of much CESIUM.) Pour the mixture through a very small filter.

Treat the filtrate by P. 170. Treat the precipitate no further.

Notes.—1. The $SbCl_3$ reagent precipitates, in the form of $3CsCl \cdot 2SbCl_3$, any cesium present in excess of about 5 mg.; while even 100 mg. of rubidium remain in solution, and 1 mg. of it is not carried down to an appreciable extent by 100 mg. of cesium. To attain this result with the cesium the volume is made small, an excess of concentrated reagent is added, and the solution is allowed to stand. The removal in this way of any large quantity of cesium enables a much more delicate test for rubidium to be made subsequently with sodium hydrotartrate (in P. 170).

2. The $SbCl_3$ reagent is a 6 f. solution of $SbCl_3$ in 6 n. HCl. The reagent is made up with HCl to avoid hydrolysis of the antimony salt.

Procedure 170.—*Separation of Rubidium from the Remaining Cesium.*—To the filtrate from the $SbCl_3$ precipitate (P. 169) add 15 cc. of water, and saturate it with H_2S gas. Filter out and reject the precipitate. Evaporate the filtrate to complete dryness. Add 1–2 cc. of water, pass in H_2S for a few moments, and pour the solution into a short pyrex test-tube (through a very small filter, if there is any residue). Evaporate the solution carefully to dryness. Cool the tube. Add 5 drops of saturated solution of sodium hydrotartrate (see

Note 4), and stir the mixture frequently for at least five minutes (unless a precipitate appears sooner); then add 0.5 cc. more, and let the mixture stand 10 minutes with frequent stirring. (Crystalline precipitate, presence of RUBIDIUM or POTASSIUM.) In case there is much precipitate, add 1.5 cc. of saturated sodium hydrotartrate solution, then 0.25 g. of finely powdered sodium hydrotartrate; and let the mixture stand with frequent stirring for 20 minutes. Filter the mixture with the aid of suction through a very small dry filter, wash the precipitate with 0.5 cc. of ice-cold saturated sodium hydrotartrate solution, using suction, and add the washings to the filtrate.

Treat the precipitate by P. 171. Treat the filtrate by P. 172.

Notes.—1. The solution is diluted with 15 cc. of water before saturating with H_2S, in order to ensure complete precipitation of the bismuth and antimony. The filtrate is then evaporated to dryness, the residue is treated with a little water and H_2S, and the solution is filtered if it is not perfectly clear.

2. To ensure the precipitation of 1 mg. or less of rubidium the dry residue is treated at first with only 5 drops of the saturated reagent, and the mixture is allowed to stand with frequent stirring. Under these conditions 1 mg. of rubidium gives almost immediately a crystalline precipitate, and even 8 mg. of cesium give no precipitate in 30 minutes (whereas not more than 5 mg. of it should be present after the treatment with $SbCl_3$). To determine whether much rubidium is present 0.5 cc. of the reagent is added. If a large precipitate results, to ensure complete removal of the rubidium 1.5 cc. more of the saturated solution and 250 mg. of the solid hydrotartrate are added. With this quantity and concentration of the salt 100 mg. of rubidium are removed to such an extent that not more than 1.5–2.0 mg. remain per cubic centimeter of solution; and this does not give a precipitate in the subsequent test for cesium. Moreover, in the presence of 100 mg. of rubidium, 1 mg. of cesium passes almost completely into the filtrate.

3. The mixture is filtered with the aid of suction, and the precipitate is washed with a little of the reagent to remove any adhering cesium salt; for this would give a precipitate that could not be distinguished from rubidium in the confirmatory test for this element (in P. 171). The washing must, however, be done

with a very small volume of ice-cold saturated reagent and this must be sucked through the filter rapidly, since rubidium hydrotartrate is fairly soluble in water. When washed in this way enough rubidium remains, when only 1 mg. is present, to give the confirmatory bismuthinitrite test in P. 171.

4. A better reagent for the detection of a small quantity of rubidium in the presence of cesium is sodium 6-chloro-5-nitrotoluenemetasulfonate; and if this is available, 1 cc. of a saturated solution of it should be substituted for the 5 drops and 0.5 cc. of saturated sodium hydrotartrate prescribed in the Procedure. It has the advantage that 0.5 mg. of rubidium gives a precipitate almost immediately, and that the precipitate with 1–2 mg. is far more voluminous than that given by the hydrotartrate. Owing to the expensiveness of the reagent and the bulkiness of the precipitate, it is somewhat less suitable for the complete precipitation of a large quantity of rubidium; this should therefore still be removed, as in the Procedure, by the subsequent addition of 1.5 cc. of the saturated hydrotartrate solution and of the powdered substance. Cesium does not give a precipitate with 1 cc. of the reagent unless more than 10 mg. is present. Potassium behaves like rubidium.

Procedure 171.—*Confirmation of Rubidium.*—Through the filter containing the hydrotartrate precipitate (P. 170) pour repeatedly a 0.5–5.0 cc. portion of 9 n. $NaNO_2$. To the solution add 3–30 drops of $Bi(NO_3)_3$ reagent, shake the mixture, and let it stand at least half an hour in a mixture of ice and water. (Yellow crystalline precipitate, presence of RUBIDIUM.)

Notes.—1. This test distinguishes rubidium from any potassium that may have been retained in the bismuthinitrite precipitate in P. 167. Cesium if present would, like rubidium, give a precipitate here (as in P. 167); but of the small quantity (5 mg.) that may not have been precipitated by $SbCl_3$ in P. 169 scarcely any will have been retained in the washed hydrotartrate precipitate in P. 170.

2. By 0.5 cc. of 9 n. $NaNO_2$ about 5 mg. of rubidium as hydrotartrate are dissolved. The acidity of the hydrotartrate solution is suitable for the precipitation of rubidium by $Bi(NO_3)_3$.

3. Regarding the conditions and delicacy of the precipitation of the rubidium by $NaNO_2$ and $Bi(NO_3)_3$, see the Notes on P. 167.

Procedure 172.—*Detection of Cesium.*—To the filtrate from the hydrotartrate precipitate (P. 170) add 3 cc. of water and 1 cc. of 1 n. silicotungstic acid, and let the mixture stand at least half an hour. (Fine white precipitate, presence of CESIUM.)

Notes.—1. Silicotungstic acid yields with 0.5 mg. of cesium a considerable precipitate, while even 8 mg. of rubidium remain dissolved under the conditions of the Procedure. The other alkali elements, sodium, lithium, and potassium, and the alkaline-earth elements give no precipitates, even if present in fairly large quantities.

2. The precipitate of cesium silicotungstate has the formula $Cs_8SiW_{12}O_{42}$. Hence the silicotungstic acid reagent probably consists, at least in part, of the complex acid $H_8SiW_{12}O_{42}$. The reagent is made up approximately 1 normal in the acid on the basis of this formula.

PART II

CONFIRMATORY EXPERIMENTS

CONFIRMATORY EXPERIMENTS

PREPARATION OF THE SOLUTION

GENERAL DISCUSSION

D. 3.—Separation of Arsenic from Antimony and Tin by Distillation of a Hydrochloric Acid Solution Containing Potassium Bromide.—See Gooch, *Methods in Chemical Analysis,* 316 (1912); Gooch and Phelps, *Am. J. Sci.* (3), **48**, 216 (1894).

Separation of Selenium from Tellurium by Volatilizing Selenium Bromide.—See Gooch, *Methods in Chemical Analysis,* 390 (1912); Gooch and Pierce, *Am. J. Sci.* (4), 1, 181 (1896); and C. E., P. 4, N. 2–3.

D. 13.—Destruction of Organic Matter.—For its destruction by nitric and perchloric acids, see C. E. on P. 1, N. 5. For its destruction by sulfuric and nitric acids, see Noyes and Bray, *J. Am. Chem. Soc.,* **29**, 153 (1907).

Volatilization of Mercury on Evaporating with Sulfuric Acid.—To 5 mg. and 100 mg. of Hg as $HgCl_2$, in separate experiments, were added 2 cc. of 16 n. HNO_3 and 2 cc. of 36 n. H_2SO_4. The mixture was evaporated to dryness, the residue being heated until the bottom of the casserole was dull red: the residue was found to contain about 0.8 mg. of Hg in the first experiment, and about 10 mg. in the second, showing that by far the larger part, but not all, of the mercury volatilized.

100 mg. of Hg as $Hg(NO_3)$, and as $HgCl_2$, in separate experiments, were mixed with 0.5 g. of K_2SO_4, 3 cc. of 36 n. H_2SO_4, 1 cc. of 16 n. HNO_3 and 5 cc. of water in a casserole, and evaporated slowly to fuming. The H_2SO_4 was fumed off, and the casserole then heated more strongly (but not quite to dull redness) until the residue was about two thirds solid at that temperature. The residue was dissolved in 10 cc. of water and 1 cc. of 6 n. HCl, and treated with H_2S: the precipitate of HgS was estimated to contain 50–60 mg. of Hg in the first experiment, and about 50 mg. of Hg in the second; showing that mercury, whether present as chloride or nitrate, volatilizes only slowly when an alkali-element is also present.

Volatilization of Germanium Chloride on Evaporating with Sulfuric Acid.—5 mg. of Ge as Na_2GeO_3 were dissolved in 0.5 cc. of cold 12 n. HCl, and added to 5 cc. of 36 n. H_2SO_4 and 0.5 cc. of 16 n. HNO_3. The mixture was heated in a covered casserole until the H_2SO_4 began to fume; the cover was removed, and the solution evaporated to about 3 cc. This was poured into 15 cc. of water, and the solution saturated with H_2S: a precipitate formed estimated to contain 1 mg. of Ge.

D. 14.—Behavior of Selenium on Distilling with Hydrochloric Acid.—See Gooch and Evans, *Am. J. Sci.* (3), **50**, 400 (1895); Gooch, *Methods in Chemical Analysis*, 385 (1912).

A solution of 100 mg. of metallic Se in 10 cc. of 6 n. HCl and 1 cc. of 16 n. HNO_3, prepared by 20 minutes' heating on a steam-bath, was distilled, till the volume became 3 cc., into 10 cc. of water; and 2–3 g. of Na_2SO_3 were added to the distillate: no precipitate formed.

Behavior of Arsenic and Germanium on Distilling with Hydrochloric Acid.—See Wada and Kato, *Sci. Papers Inst. Phys. Chem. Research*, **3**, 255–257 (1925).

Behavior of Selenic Acid with Hydrogen Sulfide.—See Mitscherlich, *Ann. Phys. Chem.* (1), **9**, 629 (1827); and Benger, *J. Am. Chem. Soc.*, **39**, 2171 (1917).

In each of five experiments a solution containing 5 mg. of Se as H_2SeO_4 was saturated with H_2S. The experimental conditions and the results are shown in the following table:

Cc. of solution	*Normal in HCl*	*Temperature*	*Time*	*Precipitate*
100	0.3	20°	1 hour	None
100	0.3	90–100°	10 min.	None
10	6.0	20°	10 min.	Turbidity, 0.2 mg. of Se
10	6.0	90–100°	10 min.	Small red, 0.5–1.0 mg. of Se
10	12.0	20°	10 min.	Yellow, 5 mg. of Se

D. 15.—Decomposition of Fluorides with Nitric Acid or with Nitric Acid and Silica.—In the experiments tabulated below the fluorides listed in the first column were freshly precipitated from nitrate solutions by HF in a platinum dish, the mixture was digested on a steam-bath, and then evaporated to complete dryness, but without heating the residue above 120°. 5 cc. of 16 n. HNO_3 were added, and the mixture was evaporated slowly to dryness. The residue was treated with 16 n. HNO_3 (sometimes with the addition of other substances as noted in the table), the mixture evaporated to dryness, and the residue digested with 10 to 20 cc. of 1 n. HNO_3. The character of the residue is noted in the second column. The solution was pipetted off, or the mixture was filtered, which was often difficult on account of the colloidal nature of the fluoride residue. The quantity of the element given in the third column was that estimated from the size of the precipitate obtained in the solution (thus on adding oxalate in the case of calcium) or by difference from the content of the residue. The quantities of the elements are in this table and in following tables expressed in milligrams.

In the experiments with silica, grouped in the second part of the table, 1 g. of pure ignited precipitated silica was added after the first evaporation with HNO_3, the residue after the next evaporation was heated for 1 hour at 120° (see C. E., D. 17), then digested with dilute HNO_3; the mixture was filtered, the silica destroyed by HF, and the size of the fluoride residue noted.

A study of all these experiments and of those with $HClO_4$, given in C. E., P. 3, N. 4, shows that the efficiency of the various processes for decomposing fluorides decreases in the order: fuming with H_2SO_4, fuming with $HClO_4$, evaporation with HNO_3 and SiO_2, evaporation with HNO_3 alone.

Substance taken	*Residue*	*Solution*	*Remarks*
50 Ca as CaF_2	None	50 Ca, small F	Filtrate clear, became turbid with NH_4OH.
500 Ca as CaF_2	220[a] Ca	280 Ca	These were the results after evaporating 10 times with HNO_3.
100 Ca as CaF_2	71 Ca 43 15[a]	29 Ca 28 28	These were the results of 3 successive treatments with fuming HNO_3.
100 Ca as CaF_2 2 g. of NH_4NO_3	30 Ca 5 0	70 Ca 25 5	These were the results of 3 successive treatments with HNO_3.
100 Sc as ScF_3	Very large	Small	Residue gave a nearly clear solution with cold 16 n. HNO_3, but not with 1 n. HNO_3.
250–500 Rare earths[b] as fluorides	Very large	Small	
500 Ca as CaF_2 1 g. of SiO_2	0 Ca	500 Ca	
50 Th as ThF_4 1 g. of SiO_2	5 Th	45 Th	Residue was estimated from its size.
250 Th as ThF_4 1 g. of SiO_2	25 Th	225 Th	Residue was estimated from its size.
100 Sc as ScF_3 1 g. of SiO_2	70[c] Sc	30 Sc	
250–500 Rare earths[b] as fluorides, 1 g. of SiO_2	0–3	Large	

[a] The residue was fumed with H_2SO_4, whereby it was completely decomposed; and the calcium was precipitated with oxalate.

[b] Separate experiments were made with 250 mg. of Y, 250 mg. of Ce, 500 mg. of Nd, and a mixture of 50 mg. of Er and 50 mg. of Y, both with HNO_3 alone, and with HNO_3 and SiO_2.

[c] The ScF_3 residue when fumed with $HClO_4$ gave a nearly clear solution, but this became very turbid when diluted. After fuming with H_2SO_4 and diluting, a clear solution resulted.

D. 16.—Volatilization of Elements from Perchloric Acid Solution with a Current of Steam and Hydrogen Chloride Gas.—In the series of experiments summarized in the tables on the following pages the quantities of various elements (obtained by evaporating stock solutions nearly to dryness) were dissolved in the "reagents added," and the solution was placed in a 50-cc. distilling flask with its bulb submerged in a paraffin ("ceresin") bath. The bath was then gradually heated to expel water and hydrobromic acid, this process constituting the "preliminary evaporation" of the table, till the temperature of the bath or the distilling liquid reached the value shown in the column headed "final bath temp." or "final liquid temp." The distillate, whose volume is shown in the table under "Cc. collected," was saturated with H_2S after proper neutralization, and any precipitates formed compared with standards, the results being shown in the column headed "Mg. found." The temperature was then rapidly raised to that shown in one of the next two columns, and maintained there within 5°, while a current of gas generated in another flask by boiling the mixture indicated under "gas generating mixture" was passed through the liquid in the distilling flask at a "rapid" or "slow" rate (corresponding respectively to the evaporation of 3–4 cc. or of 1.5–2.0 cc. per minute of the boiling liquid). The distillate was collected in 5–10 cc. of water or of 6 n. HCl. The receiver was changed after certain intervals, a star being inserted in the table when the distillate was not changed at the end of that interval. The quantities of element present in these distillates and in the liquid remaining in the flask were estimated by precipitation with H_2S after proper neutralization. The italic letters *a, b, c* . . . affixed to certain words or numbers in the tables have the following meanings:

[a] The vapors passed into the distilling flask were superheated by passing through a 150-cm. glass helix immersed in the paraffin bath.

[b] The distilling flask used in these experiments had a side-arm close above the bulb of the flask.

[c] The distillation was rapid till the first distillate was collected, and afterwards slow. At this intermediate point 3 cc. more 9 n. $HClO_4$ were added, and the generating mixture replaced by a fresh portion of it.

[d] The distillation was continued till only 0.5 cc. of residual liquid remained.

[e] The whole 15 cc. of 9 n. HBr were distilled through the mixture in 15 minutes. Then 2 cc. of 9 n. $HClO_4$ were added, and another 15-cc. portion of 9 n. HBr was distilled through the mixture in the next 15 minutes.

Element	Milligrams taken	Substance	Reagents added	Gas generating mixture	Preliminary evaporation				Subsequent distillation with HCl and steam							Milligrams in residue in flask
					Final bath temp.	Final liquid temp.	Distillate		at bath temp.	at liquid temp.	Rate	Milligrams passing during successive intervals				
							Cc. collected	Mg. found				10 min.	5 min.	5 min.	10 min.	
Sn	500	$SnCl_4$	3 cc. 9 n. $HClO_4$	H_2SO_4 and NaCl		Fuming			200°		Rapid	450	*	40		10
	500	"	"	12 n. HCl		"			"		"	500	*	0		0
	500	"	"	H_2SO_4 and NaCl		"			"		"	490	*	5	2	3
	500	"	3 cc. 9 n. $HClO_4$ 3 cc. 9 n. HBr	100 cc. 12 n. HCl	180°			300	"		Slow	*	200			0.2–0.5
	500	"	"	"	150° 180°			0 200								
	500	"	"	"		125° 140°	0.1 3–4	0 200								
	1	"	"	100 cc. 12 n. HCl					200°		Slow	0.8–0.9				0.1–0.2
Sb	5	$SbCl_3$	1 drop Br_2 3 cc. 9 n. $HClO_4$ 3 cc. 9 n. HBr	6 n. HCl	180°		4	0	200°		Slow	4.8	0			
	500	"	3 cc. 9 n. $HClO_4$ 3 cc. 9 n. HBr	100 cc. 12 n. HCl	180°			10	200°		Slow	*	370	*	60	70
	500	"	3 cc. 9 n. HBr 6 cc. 9 n. $HClO_4$ 2 drops Br_2	100 cc. 12 n. HCl		130°		25		170°	Rapid[b] Slow[c]	450	*	*	25	1
	500	"	"	125 cc. 8 n. HCl		140°		30		170°	Rapid[b] Slow[c]	425	*	*	40	10
	50	"	5 cc. 9 n. $HClO_4$ 0.5 cc. 9 n. HBr 2 drops Br_2	125 cc. 8 n. HCl						170°	Rapid[b]	*	*	49		1
	1	"	3 cc. 9 n. HBr 3 cc. 9 n. $HClO_4$	100 cc. 12 n. HCl					200°		Slow	0.8				0.2

Element	Milligrams taken	Substance	Reagents added	Gas generating mixture	Preliminary evaporation: Final bath temp.	Preliminary evaporation: Final liquid temp.	Preliminary evaporation: Distillate: Cc. collected	Preliminary evaporation: Distillate: Mg. found	Subsequent distillation with HCl and steam: at bath temp.	Subsequent distillation with HCl and steam: at liquid temp.	Subsequent distillation with HCl and steam: Rate	Subsequent distillation with HCl and steam: Milligrams passing during successive intervals: 10 min.	5 min.	5 min.	10 min.	Milligrams in residue in flask
Sb	500	Sb_2O_5	3 cc. 9 n. $HClO_4$	H_2SO_4 and NaCl		Fuming			200°		Rapid	25	*	50		425
	500	"	3 cc. 9 n. $HClO_4$ 3 cc. 9 n. HBr	12 n. HCl		Fuming			200°		Rapid	450	*	45		5
	500	$SbCl_3$	0.5 cc. Br_2 3 cc. 9 n. $HClO_4$ 8 cc. 9 n. HBr	12 n. HCl		Fuming			200°		Rapid	475	*	25		0
	500	"	6 cc. 9 n. $HClO_4$ 3 cc. 9 n. HBr	100 cc. 12 n. HCl					200°		Rapid	450	*	*	30	20
	500	"	3 cc. 9 n. HBr 4 cc. 9 n. $HClO_4$	15 cc. 9 n. HBr						170°	Slow[e]	*	489	*	10	1
Hg	100	$HgCl_2$	3 cc. 9 n. $HClO_4$	6 n. HCl	200°				200°		Slow	*	40	*	35	25
	100	$Hg(ClO_4)_2$	3 cc. 9 n. $HClO_4$ 3 cc. 9 n. HBr	6 n. HCl	200°				180–200°		"	*	*	25	50	25
	500	"	"	6 n. HCl	150°		3	0	150–200°		"	70	100	150	5	175
	500	$HgCl_2$	3 cc. 9 n. $HClO_4$	H_2SO_4 and NaCl					180°		Rapid	*	*	*	498	2
	100	"	"	12 n. HCl					180°		Slow	*	98			2
	2	"	"	"					180°		"	*	1.9			0.1
	500	"	"	"		Fuming			200°		Rapid	490	*	5		5
	100	$Hg(ClO_4)_2$	3 cc. 9 n. HBr 3 cc. 9 n. $HClO_4$	120 cc. 10 n. HCl	180°			0	200°		Slow	40	*	*	60	0[d]
	100	"	"	150 cc. 7.6 n. HCl	180°			0	200°		"	65	*	33		2
	500	"	"	"	180°			0	200°		"	*	100	Discarded		

Element	Milligrams taken	Substance	Reagents added	Gas generating mixture	Preliminary evaporation				Subsequent distillation with HCl and steam							Milligrams in residue in flask
					Final bath temp.	Final liquid temp.	Distillate		at bath temp.	at liquid temp.	Rate	Milligrams passing during successive intervals				
							Cc. collected	Mg. found				10 min.	5 min.	5 min.	10 min.	
Hg	500	$Hg(ClO_4)_2$	3 cc. 9 n. HBr 3 cc. 9 n. $HClO_4$	150 cc. 7.6 n. HCl	180°			0	200°		Slow[a]	*	200	Discarded		
	500	"	"	12 n. HCl	180°		2.5	2	200°		Slow	200	*	300		2
	500	$HgCl_2$	"	100 cc. 12 n. HCl		130°		3	220–235°	170°	Rapid[b] Slow[c]	475	*	20		0[d]
	1	"	"	"					200°		Slow	0.8				0.2
Mo	100	$(NH_4)_2$-MoO_4	3 cc. 9 n. HBr 3 cc. 9 n. $HClO_4$	6 n. HCl	160°				200°		Slow	0.9	0.6	0.5		98
	100	"	3 cc. 9 n. $HClO_4$	12 n. HCl		Fuming			"		Rapid	1	*	1		98
	100	"	3 cc. 9 n. $HClO_4$ 10 cc. 9 n. HBr	"		"			"		"	3	*	2		95
	2	"	6 cc. 9 n. $HClO_4$ 3 cc. 9 n. HBr	100 cc. 12 n. HCl		140°		0		170°	"	1.5				0.5
	1	"	"	"		140°		0		170°	"	0.7				0.3
Te	100	TeO_2	3 cc. 9 n. $HClO_4$	12 n. HCl		Fuming			180–200°		"	0	*	0		100
Ga	50	$GaCl_3$	"	"		"			"		"	0	*	0		50
Ti	100	$TiCl_4$	3 cc. 9 n. $HClO_4$ 5 cc. 9 n. HBr	"		"			"		"	0	*	0		100
Fe	500	$Fe(NO_3)_3$	3 cc. 9 n. $HClO_4$	"		"			"		"	0	*	0		500
Cd	500	$Cd(NO_3)_2$	"	"		"			"		"	0				500
Te	100	TeO_2	"	"		"			"		"	0.5	*	0.5		99
Os Ru	20 25	OsO_4 $RuCl_3$	3 cc. 9 n. $HClO_4$ 3 cc. 9 n. HBr	100 cc. 9 n. HCl	200°			1 0	200°		Slow	*	*	19 24		0.5 1

D. 17.—Behavior of Various Elements on Evaporating with Nitric Acid, Heating at 120°, and Extracting with Hot Dilute Nitric Acid.— A mixture of 1 mg. each of Ti, Ta, Cb, W, Sn, and Sb as fluorides was treated as outlined below. The residue was dissolved in HF and analyzed (by P. 31–49): distinct tests were obtained for every element except antimony.

Six separate solutions containing respectively 1 mg. of Cb, Ta, Ti, Sn, W, and Mo, along with 500 mg. Al as $Al(NO_3)_3$ in 5 cc. of 27 n. HF, were treated as outlined below: there was a distinct residue in all the cases except that of molybdenum.

In the experiments tabulated below the procedure was essentially as follows: to the substance or substances listed in the second column HNO_3 was added in large excess, and the mixture was evaporated as nearly to dryness as possible without heating the residue much above 100°. When fluorides were present this HNO_3 treatment was carried out three times in a platinum dish. The residue was heated in a hot closet at 120° for one hour, or longer if the mass was not then perfectly dry. The residue was loosened from the dish and rubbed to a fine powder with a pestle; 5 cc. of 6 n. HNO_3 were added, the dish was covered, and the mixture heated on a steam-bath for 5 minutes, 15–20 cc. of water were added, the mixture was heated to boiling and filtered. The character or content of the residue is given in the third column. Frequently the content was estimated by observing the size and character of the residue before filtration. In other cases the residue (res.) or the filtrate was subjected to an appropriate treatment, as indicated in the last column of the table. The fifth column gives the content of the filtrate. In some of the experiments the residue was heated a second time with dilute HNO_3, with the result shown in the fourth column.

Milligrams of element	Substance taken	Character or content of residue after		Content of filtrate	Remarks
		first treatment	second treatment		
100 Cb	$HCbO_3$	Large	——	0 Cb	
2 Cb 100 PO_4	Cb_2O_5 in HF Na_2HPO_4	Distinct	——	100 PO_4	
2 Cb 200 Zr	Cb_2O_5 in HF $ZrO(NO_3)_2$	Distinct	——	200 Zr	
2 Cb 100 Mo	Cb_2O_5 in HF MoO_3 in HF	2 Cb Large Mo	——	Mo	Cb in res. found by analysis.
50 Ta	$HTaO_3$	Large	——	0.4 Ta	Filtrate evaporated, ignited, weighed.
100 Ta[a]	Ta_2O_5 in HF	Large	——	0 Ta	NH_4OH gave no ppt. in filtrate.
2 Ta 100 PO_4	Ta_2O_5 in HF Na_2HPO_4	Distinct	——	100 PO_4	
2 Ta 200 Zr	Ta_2O_5 in HF $ZrO(NO_3)_2$	Distinct	——	200 Zr	
2 Ta 500 Fe	Ta_2O_5 in HF $Fe(NO_3)_3$	Distinct	——	500 Fe	
2 Ta 100 Mo	Ta_2O_5 in HF MoO_3 in HF	2 Ta Large Mo	——	Mo	Ta in res. detected by analysis.
85 Ti	H_2TiO_3	Large	——	8 Ti	Filtrate evaporated, ignited, weighed.
500 Ti 500 Zr	TiO_2 in HF $ZrO(NO_3)_3$	Large	Very small	Ti and Zr	
500 Ti 500 Zr	$TiOCl_2$ $ZrO(NO_3)_2$	Large	Small	Ti and Zr	Final res. after 4 evaporations with HNO_3 gave no test for Zr.
500 Ti 50 As	TiO_2 in HF As_2O_3	Large Ti 20 As	——	30 As	
22 Sb	Sb_2O_5	Large	——	1 Sb	Filtrate evaporated, ignited, weighed.
2 Sb	Sb_2O_5	Very slight	——	2 Sb	Distinct ppt. before diluting HNO_3.
5 Sb	Sb_2O_5	2.5 Sb	Very slight	Sb	
10 Sb	Sb_2O_5	Medium	Medium	Sb	
30 Sn	H_2SnO_3	Medium	——	0.3 Sn	Filtrate evaporated, ignited, weighed.
500 Sn	H_2SnO_3	Large	——	3 Sn	Filtrate evaporated, ignited, weighed.
750 Sn[b]	Sn	Large	——	0 Sn	Filtrate evaporated with HCl gave no ppt. with $HgCl_2$.

[a] This experiment was repeated, except that the heating at 120° was omitted: the filtrate contained much Ta, showing that dehydration is necessary.

[b] Two other experiments were made with 500 mg. of Sn as SnO_2 in HF, omitting the heating at 120°: the filtrates contained large amounts of tin. Dehydration of H_2SnO_3 is evidently necessary.

Milligrams of element	*Substance taken*	*Character or content of residue after*		*Content of filtrate*	*Remarks*
		first treatment	*second treatment*		
500 Sn 500 V	$SnCl_2$ NH_4VO_3	Large yellow	——	Sn (?) Little V	Several evaporations were made with HNO_3. Filtrate was brown, showing V. Res. with HCl gave blue-green solution showing V.
500 Sn 500 V	Sn Na_3VO_4	Large yellow	——	Medium Sn Large V	Filtrate (colored) was evaporated with HCl and tested with H_2S.
500 Sn 500 Mo	Sn Na_2MoO_4	Large	——	10 Sn Large Mo	Filtrate evaporated and fused with KCN yielded a metallic button leaving res. with HNO_3.
500 Sn 500 W	Sn Na_2WO_4	Large	——	0 Sn 0 W	Filtrate evaporated with HCl gave no blue color with Zn and no ppt. with $HgCl_2$.
500 Sn 4 W 4 PO_4	Sn Na_2WO_4 Na_2HPO_4	Large	——	10 Sn 0 W PO_4	Filtrate tested with $(NH_4)_2MoO_4$. Rest evaporated with HCl, tested for Sn with H_2S, filtered, evaporated, tested for W.
70 W	H_2WO_4	Large	——	0 W	Filtrate evaporated gave 1.1 mg. of solid, but not soluble in NH_4OH.
50 W 150PO_4	Na_2WO_4 Na_2HPO_4	None	——	50 W 150 PO_4	
5 W[c] 50 As	Na_2WO_4 Na_3AsO_4	None	——	5 W 50 As	
100 Mo	MoO_3 in HF	Medium	3 Mo	Mo	
500 Mo	MoO_3 in HF	Large	170 Mo	Mo	
50 Zr 600 PO_4	$ZrO(NO_3)_2$ Na_2HPO_4	Medium	——	Little Zr Large PO_4	
50 Zr 800 As	$ZrO(NO_3)_2$ As_2O_3	Medium	——	Large Zr Large As	
500 Zr 50 As	$ZrO(NO_3)_2$ As_2O_3	Very small	——	Large Zr Large As	
500 Zr	$ZrO(NO_3)_2$	None	——	500 Zr	

[c] For evidence that vanadic acid does not dissolve WO_3, see C. E., P. 35, N. 1.

Milligrams of element	*Substance taken*	*Character or content of residue after*		*Content of filtrate*	*Remarks*
		first treatment	*second treatment*		
50 Bi 200 Sb	$Bi(NO_3)_3$ Sb_2O_3	0 Bi Large Sb	——	50 Bi Small Sb	Res. in HCl gave no ppt. with $(NH_4)_2S$.
500 Bi 500 Sb	$Bi(NO_3)_3$ Sb_2O_3	Large Bi Large Sb	——	Large Bi Small Sb	Res. in HCl gave large black ppt. with $(NH_4)_2S$.
500 Bi	$Bi(NO_3)_3$	None	——	500 Bi	
50 Se 200 Sb	SeO_2 Sb_2O_3 in HCl	5 Se Large Sb	——	45 Se Small Sb	
50 Se 200 Sb	SeO_2 Sb_2O_3 in HCl	10 Se Large Sb	——	40 Se Small Sb	
50 Te 200 Sb	TeO_2 Sb_2O_3 in HCl	Some Te Large Sb	——	Some Te Small Sb	
50 Te 200 Sn	TeO_2 Sn	Some Te Large Sn	——	Some Te	
500 Te	TeO_2	None	——	500 Te	
76 Ge[d]	GeO_2	62 Ge	——	14 Ge	Filtrate evaporated, ignited, weighed.
62 Ge	GeO_2	42 Ge	——	20 Ge	Filtrate evaporated, ignited, weighed.
500 Th	$ThO(NO_3)_2$	None	——	500 Th	
500 Al	$Al(NO_3)_3$	None	——	500 Al	
500 Cr	$Cr(NO_3)_3$	None	——	500 Cr	
500 Pb	$Pb(NO_3)_2$	None	——	500 Pb	
75 Ga	$Ga(NO_3)_3$	None	——	75 Ga	Res. dissolved incompletely in 5 cc. of 6 n. HNO_3.
500 V	NH_4VO_3 in HF	Medium	None	500 V	
500 Fe	$FeCl_3$	Small	None	500 Fe	
20 Au	$AuCl_3$	2 Au	——	18 Au	After four evaporations with HNO_3.
400 In[e]	$In(NO_3)_3$	None	——	400 In	
50 each of Al, Ni, V, Cr, Ba, Zn		None	——	——	All dissolved in dilute HNO_3.

[d] The residue after dehydration at 120° was boiled for only one minute with 5 cc. of 6 n. HNO_3.

[e] Wada and Oto, *Scientific Papers Inst. Phys. Chem. Research*, 1, 63 (1922).

D. 18.—Precipitation of Iridium, Rhodium, Copper, and Tellurium by Boiling with Formate.—See Mylius and Dietz, *Ber. d. chem. Ges.*, **31**, 3191 (1898).

20 mg. of Ir as Na_2IrCl_6, 20 mg. of Rh as $RhCl_3$, 500 mg. of Cu as $CuCl_2$, and 200 mg. of Te as TeO_2 were separately dissolved in 35-cc. portions of 3.5 n. $NaCHO_2$, which in the separate experiments contained also enough free $HCHO_2$ to produce the normality shown in the third column of the following table. The mixtures were boiled with a reflux cooler for the times shown, and then filtered; this boiling and filtering being repeated a second time in the rhodium experiments, and a second and a third time in the iridium experiments. The milligrams of iridium and rhodium precipitated after each interval were estimated from the relative size of the different precipitates. The milligrams left in all the final solutions after the last boiling were determined by saturating them with H_2S (and heating in a pressure-bottle in the iridium and rhodium experiments), and noting the sizes of the precipitates. The results are shown in the table.

Element		*Normality of formic acid*	*After boiling*		*After further boiling*		*Solution content*	*After further boiling*		*Solution content*
Name	*Mg. taken*		*for*	*ppt.*	*for*	*ppt.*		*for*	*ppt.*	
Ir	20	0.0	½ h.	14	1 h.	4	—	3 h.	2	0
Ir	20	0.35	½ h.	14	1 h.	4	—	3 h.	2	0
Ir	20	3.5	½ h.	12	1 h.	4	—	3 h.	4	0
Rh	20	0.0	½ h.	15[a]	6 h.	5	0.3	—	—	—
Rh	20	0.35	½ h.	15[a]	6 h.	5	0.7	—	—	—
Rh	20	3.5	½ h.	12[a]	6 h.	7	0.7	—	—	—
Cu	500	3.5	4 h.	125[b]	—	—	375	—	—	—
Te	200	3.5	4 h.	100[c]	—	—	100	—	—	—

[a] The solution was deep-blue.

[b] Partly as CuCl and partly as Cu. The H_2S precipitates given by this precipitate and by the filtrate were compared.

[c] A white precipitate of H_2TeO_3 separated at the start, and this gradually darkened.

D. 19.—Precipitation of Mercury, Gold, Platinum, and Palladium by Metallic Silver.—Separate solutions containing 500 mg. of Hg, 300 mg. of Hg, 100 mg. of Au, 100 mg. of Pt, and 100 mg. of Pd were evaporated with 3 cc. of 95% H_2SO_4, and diluted to 25 cc. with water; 1 drop of 7 n. HCl and 0.5 g. of Ag were then added, and the mixture was shaken for 5 minutes. The addition of one drop of HCl and of 0.5 g. of fresh Ag and the shaking for 5 minutes were repeated as long as any darkening was perceptible. The results were as follows. With the 500 mg. of Hg the sixth portion of silver was not darkened, and the filtrate from it gave no precipitate with H_2S. With the 300

mg. of Hg the same tests showed absence of mercury after the fourth shaking. With the 100 mg. of Au the third shaking produced only a very slight darkening. With the 100 mg. of Pt the solution gave only a slight darkening to the third portion of silver added, and after four shakings it gave no color with KI. With the 100 mg. of Pd a blackening estimated to correspond to 0.5–1.0 mg. of Pd was produced in the fourth and fifth shakings; after the fifth shaking, the solution, though still slightly yellow, gave no color with KI.

Indication of Mercury, Gold, Platinum, and Palladium afforded by Darkening of the Silver.—0.5 mg. of Au, 0.5 mg. of Hg, 0.5 mg. of Pd, and 0.5 mg. of Pt in separate solutions were treated with 2 cc. of 95% H_2SO_4 and 23 cc. of water. One drop of 7 n. HCl and 0.5 g. of Ag were then added, and the flasks were shaken for five minutes. In all four cases there was produced a darkening of the silver, which was pronounced with platinum and palladium, and detectable with gold and mercury upon comparing the precipitate with the original silver.

Behavior of Tellurium, Copper, Selenium, Ruthenium, Iridium, and Rhodium toward Metallic Silver.—Separate solutions of 500 mg. of Cu, 100 mg. of Te, 100 mg. of Se, 100 mg. of Ru, 100 mg. of Ir, and 100 mg. of Rh were treated in the way described in the above experiments with the large quantities of gold-group elements. The results were as follows. With the 500 mg. of Cu there was no darkening of the Ag; and the precipitate after dissolving in HNO_3 gave no blue color with NH_4OH. With the 100 mg. of Te nearly equal amounts were deposited on the Ag in three successive shakings; and the total amount of Te precipitated in the three shakings was estimated to be 3–4 mg. With the 100 mg. of Se considerable darkening of the Ag was noticed after each of three shakings; the three Ag precipitates were united and dissolved in HNO_3; the silver was precipitated with HCl, the HNO_3 removed by evaporation, and the solution treated with H_2S: the precipitate corresponded to 15 mg. of Se. With the 100 mg. of Ru several shakings with Ag were necessary to remove traces of platinum and palladium contained in the solution; when these traces had been removed the Ag was no longer darkened after five minutes' shaking. With the 100 mg. of Rh and the 100 mg. of Ir, there was no darkening of the Ag.

Influence of Hydrochloric Acid on the Precipitation of Tellurium by Metallic Silver.—To each of three solutions containing 50 mg. of Te 3 cc. of 95% H_2SO_4 were added, and the solution was evaporated to fuming; it was diluted to 25 cc., and 0.5 g. of metallic Ag was added. To the first solution 1 drop of 7 n. HCl was added; to the second, 3 drops; and to the third, 10 drops. The three mixtures were now rotated around a horizontal shaft in a thermostat at 25° for 30

minutes, allowed to settle five minutes, and then filtered. The amount of tellurium deposited on the Ag was estimated by dissolving in HNO_3, precipitating the silver with HCl, evaporating with HCl, saturating with SO_2 gas, and heating on a steam-bath for 30 minutes. The three solutions were estimated to contain 1.5 mg., 2 mg., and 20 mg. of Te.

Influence of Time on the Precipitation of Tellurium by Metallic Silver.—To 50 mg. of Te in each of two casseroles were added 3 cc. of 95% H_2SO_4, and the solution was evaporated to fuming, diluted to 25 cc., and treated with 0.5 g. of Ag and 3 drops of 7 n. HCl. One was agitated for 30 minutes, and the other for 48 hours. The precipitates were treated as in the previous experiment: the tellurium deposited from the two solutions was estimated to be 2 mg. and 20 mg.

Precipitation of Platinum by Metallic Mercury.—10 mg. of Pt in 3 cc. of 18 n. H_2SO_4 were heated to moderate fuming; 10 cc. of water, 3 drops of 6 n. HCl, and 1 cc. of liquid Hg were added, and the mixture was shaken for one minute, allowed to stand one hour, and filtered; the filtrate was saturated with H_2S: only a small precipitate resulted, and this volatilized on heating.

100 mg. of Pt in 2 cc. of 95% H_2SO_4 were heated to fuming; 25 cc. of water, 2 drops of 12 n. HCl, and 0.5 cc. of liquid Hg were added; and the mixture was shaken 5 minutes: a black dispersed amalgam formed. This was filtered out; the filtrate was shaken 5 minutes with 2 drops of 12 n. HCl and 0.5 cc. of Hg, and filtered; and the filtrate was shaken 5 minutes with 0.25 cc. of Hg, and filtered. This third precipitate was ignited: it yielded a residue of about 0.3 mg. of Pt. The filtrate from it was treated with H_2S, and the small precipitate tested for platinum with NH_4Cl: 0.2 mg. or less was present. Therefore the platinum was nearly completely precipitated by two shakings.

5 mg. of Pt in 3 cc. of 9 n. $HClO_4$ were heated to fuming, 10 cc. of water and 0.5 cc. of Hg were added, and the mixture was shaken for 5 minutes, filtered, and saturated with H_2S: no precipitate formed.

Non-Precipitation of Copper and Tellurium by Metallic Mercury.—500 mg. of Cu and 100 mg. of Te, in separate experiments, were dissolved in 2 cc. of 95% H_2SO_4 and evaporated to fuming; 25 cc. of water, 1 drop of 6 n. HCl, and 1 cc. of Hg were added; and the mixture was shaken for 5 minutes, and filtered. The precipitate was well washed and gently ignited (to expel the Hg); and the residue was dissolved in a little HCl and HNO_3. The solution from the copper experiment was treated with NH_4OH, then with HCl and H_2S: NH_4OH gave no blue color, and H_2S gave a slight black precipitate corresponding to 0.25 mg. of Cu. The tellurium solution was made 2.7 n. in HCl, saturated with SO_2, and heated 15 minutes: no precipitate formed.

PREPARATION OF THE SOLUTION

PROCEDURES AND NOTES

P. 1, N. 4.—Destruction of Oxalate by Nitric and Perchloric Acids.—1 g. of freshly precipitated CaC_2O_4 was heated with 5 cc. of 9 n. $HClO_4$ and 1 cc. of 16 n. HNO_3 on a steam-bath: no action took place. The mixture was fumed till the volume became 3 cc., and a few drops of the mixture were withdrawn, diluted to 10 cc., and made alkaline with 6 n. NH_4OH: a large white precipitate formed. The fumed mixture was cooled somewhat, 3 cc. of 9 n. $HClO_4$ and 2 cc. of 16 n. HNO_3 were added, and the mixture was fumed until the volume became about 3 cc., cooled, diluted to 15 cc., and treated with 6 n. NH_4OH: there was no precipitate, showing complete destruction of the oxalate.

P. 1, N. 5.—Destruction of Organic Matter with Nitric and Perchloric Acids.—To the quantities of the various materials shown in the table below were added 5 cc. of 9 n. $HClO_4$ and 1 cc. of 16 n. HNO_3; the mixtures were then heated on a steam-bath, and 1–3 cc. more 16 n. HNO_3 were gradually added. Then the dishes were heated over a flame till the $HClO_4$ fumed strongly. When the liquid was not clear and light-colored, these operations were once or twice repeated. There was never any considerable action in the cold. The results of the heatings on the steam-bath and of the fumings are shown in the following table. There was no frothing, spattering, or bumping (except in the case of the paraffin); nor was there ever any explosion or even a violent evolution of gas, though when rapid action occurred it was attended with copious escape of nitrous fumes.

Material	*Grams taken*	*Action on steam-bath*	*Destruction after first fuming*	*Treatments required*
Cotton.....	0.1	Fairly rapid	Complete	One
Tobacco.....	0.2	Fairly rapid	Almost complete	Two
Filter paper.....	0.8	Fairly rapid	Almost complete	Two
Potato starch ...	0.2	Fairly rapid	Complete	One
Glycerin.....	2.5	Fairly rapid	Complete	One
Sawdust.....	1.0	Fairly rapid	Almost complete	Two
Tartaric acid....	1.2	Less rapid	Complete	One
Paraffin.....	0.5	None	Very incomplete	Three

With the paraffin little action occurred till the $HClO_4$ fumed strongly, when charring suddenly began. A subsequent treatment with HNO_3 on the steam-bath had no apparent effect, but the charred material was gradually destroyed by adding 16 n. HNO_3, 1 cc. at a time, to the somewhat cooled mixture, and heating it at once over the flame. In two separate experiments complete destruction was attained after three such fumings.

In the experiments with filter-paper 0.1 g. of $KClO_3$, and in that with starch 0.2 g. of $KClO_3$ and 0.2 g. of NaCl, were added to determine whether explosions might be thereby produced; but these additions appeared to have no effect.

Volatilization of Mercury, Osmium, and Ruthenium on Evaporating with Nitric and Perchloric Acids.—See C. E., P. 5, N. 10, 4–5, 7–8.

P. 1, N. 6.—Explosions with Fuming Perchloric Acid.—A cold solution containing about 3 cc. of 9 n. $HClO_4$ and 10 cc. of 95% C_2H_5OH was saturated completely with dry HCl gas; the solution was evaporated over a small flame: when it became concentrated a violent explosion occurred.—The experiment was repeated 5 or 6 times except that the cold solution was diluted 2 or 3 fold and heated 15 to 30 minutes before the evaporation: in two cases, at about the time strong fuming began, there was a violent explosion which shattered the casserole and bent the iron rod of the ring stand; but in the remaining experiments, which were thought to be exactly similar, there was no explosion and the $HClO_4$ was expelled by fuming.

500 mg. of Sb as Sb_2O_3 were moistened with water, 3 cc. of 9 n. $HClO_4$ were added, and the mixture was evaporated to strong fuming in an open casserole supported on a wire gauze over a gas flame: in one of two experiments there was a violent explosion which shattered the casserole.—The experiment was repeated several times, except that the Sb_2O_3 was first heated with concentrated HNO_3, or with HBr and HNO_3: in no case was there evidence of violent reaction even when the fuming with $HClO_4$ was continued for some time.

P. 2, N. 1.—Solvent Action of Hydrobromic Acid and Bromine.—500 mg. of finely divided Cu were treated with 10 cc. of 9 n. HBr: no reaction occurred. 15 drops of Br_2 were added, and the mixture was digested on a water-bath for 10 minutes: all the metal had dissolved.

500 mg. of finely divided Pb were similarly treated: some of the metal slowly dissolved in the HBr alone, and the remainder quickly dissolved on the addition of Br_2.

500 mg. of granulated Sn were digested on a steam-bath for 5 to 6 minutes with 10 cc. of 9 n. HBr: it completely dissolved.

500 mg. of Sb as Sb_2O_3 were shaken with 10 cc. of 9 n. HBr for several minutes in the cold: it all dissolved.

500 mg. of Sn as SnO_2 previously ignited for 3 hours at a low red heat were boiled for 10 minutes with 10 cc. of 9 n. HBr with a reflux condenser: there was a large residue. The liquid was then distilled down to 3 cc., and the mixture was filtered: a residue containing a small part of the substance remained. The filtrate was diluted, nearly neutralized, and saturated with H_2S: a precipitate estimated to correspond to 350 mg. of Sn resulted.

400 mg. of Sn as precipitated SnS_2 were boiled 10 minutes with 10 cc. of 9 n. HBr with a reflux condenser, and the gases evolved were passed into 10 cc. of saturated Br_2 solution in a U-tube: in the U-tube the Br_2 was quickly decolorized, and a turbidity of sulfur formed; in the flask there was a small fine yellow residue. Then 0.5 cc. of liquid Br_2 was added to the flask, and the mixture heated on a water-bath for 10 minutes: only a turbidity remained.

That anhydrous $Cr_2(SO_4)_3$ is slowly dissolved by 9 n. HBr is shown in C. E., P. 8, N. 2.

P. 2, N. 2.—Occurrence of Selenides and their Decomposition by Acids.—See Treadwell-Hall, *Qualitative Analysis,* 5th Ed., 552 (1921); Roscoe and Schorlemmer, *Treatise on Chemistry,* 1, 467, 473 (1920).

Occurrence of Tellurides and their Decomposition by Acids.—See Roscoe and Schorlemmer, *Treatise on Chemistry,* 1, 483, 488 (1920); Ernyei, *Z. anorg. Chem.,* **25**, 313 (1900); and Hempel and Weber, *ibid.,* **77**, 48 (1912).

P. 2, N. 3.—Behavior of Decomposable Silicates on Boiling with Hydrobromic Acid.—1 g. of powdered Na_2SiO_3 was boiled 10 minutes with 10 cc. of 9 n. HBr with a reflux condenser; the solution was filtered, the filtrate evaporated, the residue heated with 16 n. HNO_3, then ignited, and boiled with 5 cc. of water and 1 cc. of 6 n. HNO_3: there was a very slight residue (apparently less than 0.5 mg.) showing that the silicic acid had been rendered almost entirely insoluble.

P. 2, N. 4.—Concentration of Hydrobromic Acid Solution from 7-Normal to 9-Normal by Boiling.—100 cc. of 7.5 n. HBr (s. g., 1.42) were slowly distilled first till 70 cc., and then till 55 cc., were left in the flask; after cooling the specific gravities were determined (1.465 and 1.474), and these were plotted against volumes of the residual solutions: it was concluded that in concentrating the 7 n. HBr to two thirds of its volume, it had become about 8.6 n.

P. 2, N. 5.—Solubility of Silver and Lead Bromides in Concentrated Hydrobromic Acid.—100 mg. of Ag as $AgNO_3$ were added to 10 cc. of 9 n. HBr: AgBr immediately precipitated, but redissolved on gentle heating. The mixture was evaporated to 6 cc.: AgBr then began to precipitate.

500 mg. of Pb as $PbBr_2$ were added to 10 cc. of 9 n. HBr, and the solution boiled down to 3 cc.: no $PbBr_2$ separated from the boiling-hot solution.

P. 3, N. 2.—Decomposition of Minerals by Nitric and Hydrofluoric Acids.—1 g. of each of the following minerals, in the form of an impalpable powder, was treated by the following process. [This process

differs from that of P. 2–6 in that it employs HNO_3 in place of HBr and Br_2, and HNO_3 and SiO_2 in place of $HClO_4$ at the end (see D. 15). It is certainly in general less, rather than more, effective for decomposing refractory materials.]

The material was first digested with 6 n. HNO_3 as long as action appeared to be taking place, and the mixture was filtered. The HNO_3 solution was evaporated just to dryness and heated at 120° for 1 hour or longer. The material undissolved by 6 n. HNO_3 was digested with 24 n. or 27 n. HF, and the fluorides decomposed by evaporation with HNO_3 or HNO_3 and SiO_2 (as described in D. 15); and the residue was heated at 120°. The two residues that had been so heated were digested with 5 cc. of 6 n. HNO_3, 20 cc. of water were added, and the mixture was heated to boiling and filtered. The residue was then treated with HF (as in P. 7, to dissolve the tungsten and tantalum groups). The results are shown in the next two paragraphs.

Each of the following materials dissolved completely, or left only a very small residue amounting to 1–5 mg.: magnetite (Fe_3O_4), menaccanite ($FeTiO_3 \cdot Fe_2O_3$), pyrite (FeS_2), pyrrhotite (Fe_7S_8), chalcopyrite ($CuFeS_2$), stibnite (Sb_2S_3), niccolite (NiAs), fluorite (CaF_2), cryolite (Na_3AlF_6), gypsum ($CaSO_4$), wollastonite ($CaSiO_3$), tremolite ($(Ca, Mg)SiO_3$), hornblende ($CaMg_2Al_2Si_4O_{12}$), titanite ($CaTiSiO_5$), orthoclase ($K_2Al_2Si_6O_{16}$), labradorite ($(Ca, Na_2)Al_2Si_3O_{10}$), garnet ($(Ca, Mg, Mn, Fe)_3Al_2Si_3O_{12}$), gadolinite ($(Y, Ce, Be, Fe)_3SiO_5$), scheelite ($CaWO_4$), columbite ($Fe(Cb, Ta)_2O_6$), samarskite ($(Fe, Y, VO_2)_5(Cb, Ta)_4O_{15}$); also the rocks basalt, obsidian, and lava.

Each of the following materials left a large residue, amounting in general to at least half of the original materials: barite ($BaSO_4$), cyanite (Al_2SiO_5), tourmaline (Al_2O_3, RO, R_2O, B_2O_3, SiO_2, F), beryl ($Be_3Al_2Si_6O_{18}$), chromite ($FeOCr_2O_3$), emery (Al_2O_3), rutile (TiO_2), zircon ($ZrO_2 \cdot SiO_2$), cassiterite (SnO_2), monazite (Ce_2O_3, La_2O_3, ThO_2, P_2O_5), molybdenite (MoS_2).

Behavior of Various Materials with Sulfuric and Hydrofluoric Acids.—See Noyes and Bray, *J. Am. Chem. Soc.*, **29**, 155–157 (1907).

Precipitation of Fluorides by Hydrofluoric Acid.—See C. E., P. 7, N. 4.

To separate 5-cc. portions of 24 or 27 n. HF were added, 0.5 mg. at a time in 1% solution (hence 0.05 cc. at a time), the elements named below until after waiting for 2–3 minutes a permanent precipitate resulted. The number of milligrams that had to be added were: Li, 5; Mg, 5; Ca, 0.5; Sr, 8; Ba, 30; Pb, 0.5; Bi, 0.5; Th, 0.5; Ce, 0.5; Pr, 0.5; Nd, 0.5; La, 0.5; Y, 0.5; and Er, 0.5.

To 5 cc. of 27 n. HF diluted with 40 cc. of water, Pb as $Pb(NO_3)_2$ was added, 1 mg. at a time, till a permanent precipitate formed: 12 mg. were required.

To 5 cc. of 27 n. HF and 25 cc. of water a 1% solution of Bi as $Bi(NO_3)_3$ was added, 1 mg. of Bi at a time, until a permanent precipitate formed: 6 mg. of Bi were required.

Solubility of the Precipitated Fluorides of Lead, Aluminum, Magnesium, Calcium, Thorium, and Cerium in Dilute Nitric Acid.—In six separate experiments 500 mg. of the elements named below as nitrate in 2 to 5 cc. of water were heated on a steam-bath with 10 cc. of 27 n. HF for 15 minutes: a large white precipitate separated in each case. 15 cc. of 6 n. HNO_3 were added to the hot mixture; and, except in the experiments with Pb and Mg, the heating was continued for 2 minutes; then the hot mixtures were filtered, the filtrates were evaporated to dryness, and the contents estimated, with results as follows: Pb, 500 (the HNO_3 solution being perfectly clear); Al, 420; Mg, 2 (estimated as $MgNH_4PO_4$); Ca, Th, and Ce, none (tested with HF).

P. 3, N. 4.—Decomposition of Calcium, Thorium, and Cerium Fluorides with Perchloric Acid.—To 300 mg. of Ca as $Ca(NO_3)_2$ were added 3 cc. of 9 n. $HClO_4$; the mixture was evaporated to fuming and cooled, and 3 cc. of 27 n. HF were added; the mixture was slowly evaporated to moderate fuming and heated at this temperature: in 2 minutes the CaF_2 had dissolved completely.

To 500 mg. of Ca as the finely powdered mineral fluorite (CaF_2) 5 cc. of 16 n. HNO_3 were added, the mixture was evaporated to dryness, the residue was boiled with 5 cc. of 12 n. HCl and 2 cc. of 16 n. HNO_3; 3 cc. of 9 n. $HClO_4$ were added, and the mixture was evaporated to fuming; 3 cc. of 27 n. HF were added, the mixture was slowly evaporated to fuming and heated at that temperature for 15 minutes, more $HClO_4$ being added from time to time; finally, the $HClO_4$ was fumed off, and the residue digested with 5 cc. of water: a small residue remained. This was filtered off, washed with water and transferred to a platinum dish, and HF was added drop by drop: the residue dissolved completely with evolution of a gas, thus showing it to be silica.

200 mg. of Th as $Th(NO_3)_4$ were digested on a steam-bath with 10 cc. of 27 n. HF for 10 minutes, 3 cc. of 9 n. $HClO_4$ were added, and the mixture was evaporated to fuming; the platinum dish was covered, and the mixture was digested for 6 minutes at such a temperature that the $HClO_4$ fumed moderately; 10 cc. of water were added, and the mixture was digested on a steam-bath for 10 minutes; the small residue was filtered off and weighed: it contained 6 mg. of ThF_4, showing

that the ThF_4 had been decomposed almost completely by the fuming $HClO_4$.

100 mg. of Th as precipitated ThF_4 were heated in a platinum dish with 3 cc. of 50% $HClO_4$ just to fuming for 20 minutes and to strong fuming for 10 minutes; then water was added: complete solution did not result at any time during this treatment, and after cooling much precipitate settled out. The mixture was filtered, and the filtrate was treated with NH_4OH: 30–40 mg. of Th were found present. The residue from the $HClO_4$ solution was again heated as before with 3 cc. of 50% $HClO_4$: a small residue estimated to contain 2–3 mg. of Th remained. The mixture was filtered, and the filtrate treated as before: the precipitate was estimated to contain 40–50 mg. of Th. The residue from the second $HClO_4$ treatment was further heated with 3 cc. of $HClO_4$: it failed to dissolve even on prolonged heating.

100 mg. of Ce as CeF_3 treated with 3 cc. of 50% $HClO_4$ were heated just to fuming for 10 minutes, and then to strong fuming for 5 minutes: most of the fluoride had dissolved. The solution was poured through a filter, and the residue was again heated with 3 cc. of $HClO_4$: a clear solution resulted after short heating.

Volatility of Boron Fluoride.—To 1 g. of H_3BO_3 5 cc. of 27 n. HF and 5 cc. of 16 n. HNO_3 were added, and the solution was evaporated to dryness on a steam-bath: no residue was left.

P. 3, N. 5.—Volatilization of Fluorides of Columbium, Tantalum, and Titanium.—According to Von Haagen and Smith, *J. Am. Chem. Soc.*, 33, 1504 (1911), columbium, tantalum, and titanium are volatilized rapidly and completely as fluorides when Cb_2O_5, Ta_2O_5, and TiO_2 are heated to a low red heat in a current of HF.

In three separate experiments 2 mg. of Cb as CbF_5 were evaporated (1) with 3 cc. of 9 n. $HClO_4$ to strong fuming; (2) with 3 cc. of 9 n. HBr to 0.5 cc., then with 3 cc. of 9 n. $HClO_4$ to strong fuming; and (3) with 3 cc. of 9 n. HBr and 3 cc. of 9 n. $HClO_4$: on diluting with water and heating, a distinct white precipitate resulted in the first and third cases, but not in the second, showing that when evaporated with HBr alone CbF_5 is volatilized. See also C. E., P. 47, N. 2.

2 mg. of Ta as Ta_2O_5 were dissolved in 5 cc. of 24 n. HF, heated on a steam-bath in a covered dish for 15 minutes, and evaporated, in one experiment twice with the addition of 2 cc. of 16 n. HNO_3, and in another experiment once without this addition. The residue was tested for tantalum by the oxyfluoride test (P. 47): the test was satisfactory in the first case, but failed in the second.—To 19 mg. of ignited Ta_2O_5 in a platinum dish 3 cc. of 27 n. HF were added, the

solution was evaporated to dryness, and the residue ignited and weighed: the loss in weight was 6 mg.

1 mg. of Ti as H_2TiO_3 was dissolved in 5 cc. of 24 n. HF, and the solution evaporated to dryness, in one experiment twice with the addition of 2 cc. of 16 n. HNO_3, and in another experiment once without this addition: the residues were tested for titanium with H_2O_2 and HCl: at least 0.5 mg. of Ti was found in the first case, and none in the second.

P. 3, N. 6.—Action of Fuming Perchloric Acid on Platinum Dishes.—3 cc. of 9 n. $HClO_4$ were evaporated to fuming in a platinum dish, and the temperature was so maintained that the acid fumed moderately for 10 minutes; 10 cc. of water and a few drops of 6 n. HCl were added, and the mixture was saturated with H_2S and allowed to stand: no precipitate was visible. Then 0.1 mg. of Pt was added: an immediate precipitate appeared, showing that the conditions for precipitating platinum were delicate.

The experiment was repeated, except that 100 mg. of Ag as precipitated AgBr were added to the $HClO_4$ at the start, and that after the fuming and diluting, the undissolved AgBr was filtered out, and the dissolved silver (amounting to 25–30 mg.) precipitated by adding 1–2 cc. of 6 n. HCl; the precipitate was filtered out, and the filtrate saturated hot with H_2S; a black precipitate formed corresponding to 0.05 mg. of Pt.

P. 4, N. 2, 3.—Behavior of Elements on Distilling with Hydrobromic Acid.—For references to the work of Gooch and his associates, see C. E., D. 3.—See also Wada and Kato, *Sci. Papers Inst. Phys. Chem. Research*, **3**, 250–253 (1925).

Various quantities of various elements, as shown in the first two columns of the table on page 292, in the form of soluble compounds, were added to 10 cc. of 9 n. HBr (s. g., 1.48) (together with a few drops of liquid Br_2 in those cases where the element might possibly be oxidized by it), and the mixture was distilled in a distilling flask, as described in P. 4, till about 3 cc. of liquid remained. The distillate (dist.) or residue (res.) were then tested for the element in the way shown in the last column, with the results shown in the third and fourth columns. In some of the experiments the residue was then evaporated to about 0.5 cc. by passing a rapid current of air through the flask immersed in boiling water, and the contents of the residue and the distillate again determined.

Reduction of Osmium Tetroxide by Hydrobromic Acid.—To 50 mg. of Os as OsO_4 in 10 cc. of water in a 50-cc. distilling flask 3 cc. of 9 n. HBr were added, and the solution was brought to a boil: much of the

Element	Milligrams taken	Milligrams present after				Method of testing
		distilling to 3 cc.		evaporating to 0.5 cc.		
		distillate	residue	distillate	residue	
As	500	496[a]	4	—	0.5	Res. with H_2S.
Se	0.5	0.5	0	—	—	Dist. with SO_2 and KI.
Se[b]	50	50	0	—	—	Res. with SO_2 and KI.
Se[c]	20	20	0	—	—	Dist. and res. with SO_2 and KI.
Ge	25	23.5	1.5	—	—	Res. with K_2CO_3 and HF after fuming with HNO_3.
Sn[d]	400	11	389	349	40	Dist. with H_2S.
Sn	500	8	492	175	317	Dist. with H_2S.
Sb	5	—	—	0.3[e]	4.7	Res. and dist. with H_2S.
Sb	50	0	50	—	—	Dist. with H_2S.
Sb	500	1.5	498	15	483	Dist. with H_2S.
Sb	575	6	569	—	—	Dist. with H_2S.
Sb[f]	500	10	490	—	—	Dist. with H_2S.
Hg	50	0	50	—	—	Dist. with H_2S.
Hg	200	0	200	0[g]	200	Dist. with H_2S.
Hg	500	0	500	—	—	Dist. with $SnCl_2$ after neutralization.
Ga	25	0	25	0	25	Dist. evaporated with fuming HNO_3.
Te	500	0	500	0	500	Dist. with SO_2.
In	50	0	50	—	—	Dist. with $(NH_4)_2S$.
In	400	0	400	—	—	Dist. with $(NH_4)_2S$.
Ti	500	0	500	—	—	Dist. with NH_4OH.
Zr	500	0	500	—	—	Dist. with NH_4OH.
Fe	500	0	500	—	—	Dist. with $(NH_4)_2S$.
U	500	0	500	—	—	Dist. with $(NH_4)_2S$.
V	250	0.5[h]	250	—	—	Dist. with NH_4OH and H_2S.
Os[i]	5	0	5	—	—	Dist. with H_2S.
Os[i]	10	0	10	0	10	Dist. with H_2S.
Ru	50	0	50	0	50	Dist. absorbed in NaOH, colorless.
Ta[k]	50	0	50	—	—	Dist. with NH_4OH.
Cb[k]	50	0	50	—	—	Dist. with NH_4OH.

[a] Three fourths of this came over with the first 3 cc. of distillate.
[b] As SeO_2, no Br_2 being added.
[c] As H_2SeO_4.
[d] This was distilled with 10 cc. of 9 n. HBr and 0.5 cc. of 9 n. $HClO_4$.
[e] Solution was boiled down in a water-bath by reducing the air-pressure.
[f] As Sb_2O_3, no Br_2 being added.
[g] On heating the residue on an asbestos mat in a rapid current of air till the volume became 0.1 cc., 10 mg. of Hg passed over.
[h] Probably carried over mechanically.
[i] As OsO_4. Distillate was absorbed in NaOH.
[k] As gently ignited Ta_2O_5 or Cb_2O_5.

OsO_4 distilled over at once; showing that the reduction of OsO_4 by 2 n. HBr is slow. The distilling flask was quickly cooled, 20 mg. of Os as OsO_4 were added, the receiver was charged with a fresh portion of NaOH, and the distilling flask was gently heated for a few minutes, the upper portion being kept cool so that nothing distilled; then the solution was vigorously boiled for one minute: no more osmium volatilized (showing that its reduction was complete).

P. 4, N. 4.—Colors Given to Concentrated Hydrobromic Acid.—The statements of this note are based on direct experiments.

P. 4, N. 5.—Behavior of Silver, Lead, and Barium on Concentrating their Hydrobromic Acid Solutions.—As to AgBr and $PbBr_2$ see C. E., P. 2, N. 5.

500 mg. of Ba as $Ba(NO_3)_2$ were added to 10 cc. of 9 n. HBr, and the solution boiled down to 3 cc.: a white precipitate separated.

P. 5, N. 2.—Decomposition of Hydrobromic Acid by Nitric Acid.—To 3 cc. of cold 9 n. HBr in a distilling flask 4 cc. of 16 n. HNO_3 were added: there was no color change. The mixture was slightly warmed: the mixture became dark-brown. It was boiled: during the first minute much Br_2 distilled, but afterwards the vapors were colorless.

P. 5, N. 3, 9.—Salts of Octivalent Osmium or Ruthenium.—See v. Wartenberg, *Ann. Chem.*, 440, 97 (1924); Krauss and Wilken, *Z. anorg. allgem. Chem.*, 145, 151 (1925).—Krauss, *ibid.*, 119, 217 (1921); 131, 348 (1923); 136, 62 (1924).

P. 5, N. 4, 5.—Behavior of Osmium on Distillation with Nitric Acid. Absorption in Sodium Hydroxide Solution and Color of the Distillate.—To 30 mg. of Os (in the trivalent or quadrivalent state) in 1 cc. of 9 n. HBr in a distilling flask with a cork stopper were added 10 cc. of 6 n. HNO_3; three successive 2-cc. portions of the liquid were distilled over into 10-cc. portions of 6 n. NaOH, and these were then treated with H_2S: the three distillates were estimated to contain 28 mg., 1.0 mg., and 0.5 mg. of osmium. To the residual liquid in the distilling flask was added 1 cc. of 0.2 f. $KMnO_4$, and the mixture was boiled for a few minutes: the distillate was estimated to contain 0.5 mg. of Os. (This apparently slow distillation of small quantities of osmium may well have been due to reduction of the OsO_4 vapors by the cork stopper; for over 90% of the osmium came over in the first period of distillation, and a complete removal was rapidly attained in the following similar experiments with a glass-stoppered flask.)

1 mg. of Os in 0.5 cc. of 9 n. HBr and 8 cc. of 6 n. HNO_3 was distilled in a glass-stoppered flask into 10 cc. of 6 n. NaOH to which 0.5 cc. of solid Na_2O_2 had been added, till 4 cc. passed over: the distillate was orange-yellow, the color being like that produced by 0.06

cc. of Br_2 in 100 cc. of water. To it was added 0.5 cc. more Na_2O_2: the color did not change. 2 cc. of water were poured into the flask, and 2 cc. of liquid were distilled into a fresh portion of NaOH: the distillate was colorless.

The experiment was repeated, using 50 mg. of Os (in place of 1 mg.), and distilling off 5 cc. at first (instead of 4 cc.): the first distillate was deep-orange; the second distillate had a very slight yellow color corresponding to only 0.1 mg. of Os. The residual liquid in the flask was neutralized and treated with C_2H_5OH and H_2S: no precipitate formed.

To 10 mg. of Os as OsO_4 were added 0.5 cc. of 9 n. HBr, 5 cc. of 6 n. HNO_3, and 3 cc. of 9 n. $HClO_4$; and the solution was distilled for 6 minutes down to 5 cc., the vapors being passed successively into 10-cc. and 20-cc. portions of 6 n. NaOH. H_2S was passed into these NaOH solutions: an immediate flocculent black precipitate formed in the first, but none in the second, showing that the first 10 cc. of 6 n. NaOH had completely absorbed the OsO_4 vapors. Two successive 1-cc. portions of 16 n. HNO_3 were now added to the residual solution, and the mixture distilled to fuming after each addition into fresh NaOH solution: the distillates were colorless and gave no precipitate with H_2S, and the residual solution was tested and found to contain no osmium (showing that all of it distilled over during the first treatment with HNO_3).

P. 5, N. 5.—Effect of Sodium Peroxide on the Color of Sodium Hypobromite.—The Br_2 produced by distilling 3 cc. of 9 n. HBr with 4 cc. of 16 n. HNO_3 was absorbed in 10 cc. of 6 n. NaOH: a yellow solution resulted. To the ice-cold solution 0.5 cc. of Na_2O_2 powder was added, and the mixture shaken: the yellow color remained, and the Na_2O_2 nearly all dissolved. 0.5 cc. more Na_2O_2 was added: the mixture became colorless almost immediately and much of the Na_2O_2 remained undissolved.

P. 5, N. 6.—Non-Precipitation of Osmium by Ethyl Alcohol.—To a distillate collected in 10 cc. of 6 n. NaOH obtained in an experiment with 50 mg. of Os, 1 cc. of C_2H_5OH was added: no precipitate formed.

To 5 mg. of Os in 10 cc. of 6 n. NaOH was added 1 cc. of 95% alcohol: the color of the solution became a very faint pink, but no precipitate formed even on standing 30 minutes. The experiment was repeated with 25 mg. of Os: the result was the same, except that the pink color was more distinct.

P. 5, N. 6.—Precipitation of Osmium by Hydrogen Sulfide.—To 10 cc. of 1 n. NaOH solution was added 0.5 mg. of Os as OsO_4: the solution had a distinct yellow color. A moderate current of H_2S was passed through the solution for 30 seconds: a colloidal black solution

formed. The solution was neutralized with 6 n. HCl and 1 cc. was added in excess: the precipitate rapidly coagulated.

P. 5, N. 7, 8.—Distillation of Ruthenium with Nitric and Perchloric Acids. Color of the Distillate Collected in Sodium Hydroxide Solution.—To 50 mg. of Ru as $RuCl_3$ in a distilling flask with a glass stopper carrying a safety-tube were added 0.5 cc. of 9 n. HBr and 8 cc. of 6 n. HNO_3; and the mixture was distilled, till 5 cc. had passed over, into 10 cc. of 6 n. NaOH, to which 0.5 cc. of solid Na_2O_2 was added, in a test-tube surrounded by cold water: the distillate remained colorless, showing that no ruthenium had distilled. To the flask were added 3 cc. of 9 n. $HClO_4$, and the mixture was distilled till 2–3 cc. remained, into a fresh 10-cc. portion of 6 n. NaOH: the distillate had an orange color corresponding to 5–10 mg. of Ru. Into the flask were poured 2 cc. more 9 n. $HClO_4$, and the mixture was again boiled down to 2–3 cc.: the distillate became almost black. 2 cc. more 9 n. $HClO_4$ were added, and the mixture again distilled down to 2–3 cc. into a fresh 10-cc. portion of 6 n. NaOH: the distillate had a yellow color corresponding to 0.8 mg. of Ru. The residue in the flask was purplish-red (probably due to an impurity); to it were added 2 cc. of 0.2 f. $KMnO_4$, and the mixture distilled into 10 cc. of 6 n. NaOH till 2 cc. passed over: the distillate had no color (showing that the ruthenium had come over in the $HClO_4$ distillations).

To 1 mg. of Ru as $RuCl_3$ in a glass-stoppered distilling flask 5 cc. of 6 n. HNO_3 and 5 cc. of 9 n. $HClO_4$ were added, and the mixture distilled into 10 cc. of 6 n. NaOH till 3 cc. remained: the distillate had an orange-yellow color (like that given by 0.1 cc. of liquid Br_2 to 100 cc. of water). 2 cc. more 9 n. $HClO_4$ were added, and the mixture distilled down to 3 cc. into fresh 6 n. NaOH; the NaOH remained colorless.

5 mg. of Ru as $RuCl_3$ were added to 5 cc. of 16 n. HNO_3 in a distilling flask with a cork stopper, and 3.5 cc. of the solution were distilled into 10 cc. of 6 n. NaOH: no color resulted. To the flask were then added 4 cc. of 12 n. HCl and 2 cc. of 16 n. HNO_3, and 3.5 cc. of the solution were again distilled into 10 cc. of 6 n. NaOH: no color formed in the distillate showing that the ruthenium had not been oxidized even by the HNO_3 and HCl.

To 10 mg. of Ru as $RuCl_3$ in a distilling flask with a cork stopper were added 5 cc. of 16 n. HNO_3; and 3.5 cc. of the solution were distilled off in about 5 minutes into a receiver containing 5 cc. of 6 n. HCl and 5 cc. of 95% alcohol: no color resulted in the distillate (showing that the ruthenium had not been oxidized). Upon adding 2 cc. of 0.2 $KMnO_4$ to the distilling flask and again distilling for a few minutes the HCl-C_2H_5OH distillate quickly became orange-red.

P. 5, N. 9.—Precipitation of Ruthenium by Ethyl Alcohol.—To 5 cc. of 6 n. NaOH and 0.3 cc. of Br_2 were added 0.5 mg. of Ru as $RuCl_3$: an orange color resulted (showing that the ruthenium was oxidized). To this solution was added 1 cc. of 95% C_2H_5OH: the orange color changed to a turbid green, and a greenish-black precipitate slowly coagulated.

2 mg. of Ru as $RuCl_3$ were added to 10 cc. of 6 n. NaOH and 0.25 cc. of Br_2, and 1 cc. of 95% C_2H_5OH were added: a dark greenish turbidity was produced almost at once, and a coagulated precipitate formed within one minute.

1 mg. of Ru was distilled from fuming $HClO_4$ into 10 cc. of 6 n. NaOH, and to the distillate 1 cc. of C_2H_5OH was added: after two minutes a greenish-black gelatinous precipitate had formed. 0.5 cc. of Na_2O_2 powder was added, and the mixture was heated: the precipitate remained.

P. 5, N. 10.—Volatilization of Mercuric Bromide on Heating with Perchloric Acid.—The quantities of mercury and the amounts of acid shown in the table were heated in a 50-cc. distilling flask. The residual liquid was then subjected to one or more further treatments as indicated. The acid was considered to be "fuming" when the vapor completely filled the flask and copious white fumes were emitted from the neck. The distillate, which was acid, was heated with H_2S. The last column shows the results.

Expt.	*Mercury taken*	*Acid added*	*Degree of heating*	*Hg in distillate*
1	5 mg. as $HgCl_2$	0.5 cc. 9 n. HBr, 4 cc. 9 n. $HClO_4$	Just to fuming	0.1 mg.
2	Residue from expt. 1	1 cc. 16 n. HNO_3	Distilled for a few seconds after fuming	0.4 mg.
3	5 mg. as $HgCl_2$	0.5 cc. 9 n. HBr, 8 cc. 6 n. HNO_3	Boiled until 3 cc. distilled	None
4	Residue from expt. 3	3 cc. 9 n. $HClO_4$	Just to fuming	None
5	Residue from expt. 4	None	Distilled a few seconds after fuming	0.2 mg.
6	Residue from expt. 5	None	Distilled 5–10 minutes	None
7	500 mg. as $HgCl_2$	0.5 cc. 9 n. HBr, 3 cc. 9 n. $HClO_4$, 1 cc. 16 n. HNO_3	Just to fuming	20 mg.

These results show that, when the mercury is present as $HgBr_2$, a small part of it is volatilized at the beginning of the distillation, but that none comes over later.

Volatilization of Mercuric Chloride on Heating with Perchloric Acid.—In each of the following experiments, to a solution of $HgCl_2$ were added 0.2–1.0 cc. of 12 n. HCl, 0.2–1.0 cc. of 6 n. HNO_3, and 3 cc. of 9 n. $HClO_4$; the mixture was heated to fuming in a casserole, and slowly evaporated as described in the table; the residue was treated with water, HCl, and H_2S, to estimate the amount of mercury that remained.

Mg. of Hg taken	*Fuming continued*	*Milligrams of mercury*	
		in residue	*volatilized*
3	10 min., just to dryness	2	1
5	10 min., to 0.5 cc.	2	3
5	10 min., to dryness	1	4
100	To first strong fuming	90–100	10–0
100	10 min., just to dryness	20	80
100	Just to dryness	20	80

Comparison of the last three experiments shows that the mercury, when present as $HgCl_2$, is volatilized to a large extent only when the evaporation is long continued.

Volatilization of Mercuric Chloride by Evaporation with Nitric Acid and Heating at 125°.—See Noyes and Bray, *J. Am. Chem. Soc.*, 29, 153 (1907). See also C. E., P. 9, N. 3.

P. 6, N. 2.—Action of Perchloric Acid on Silver Halides.—100 mg. of Ag as AgBr in 0.5 cc. of 9 n. HBr and 8 cc. of 6 n. HNO_3 were evaporated in a distilling flask to 4 cc. Then 5 cc. of 9 n. $HClO_4$ were added, and the mixture distilled until only 3 cc. of liquid remained; the mixture was filtered, and the filtrate diluted and treated with HCl: a precipitate corresponding to 30–40 mg. of Ag resulted. The residue of unattacked AgBr was put through the treatment again except that the mixture was gently boiled (but without distilling) until the AgBr had entirely dissolved: this took 20 minutes.

100 mg. of Ag as AgBr were heated in a platinum crucible with 3 cc. of 9 n. $HClO_4$ until the acid fumed strongly; the flame was then turned down so as to just maintain the fuming temperature, and kept there for 10 minutes: a faint dark-yellow color was observed at the surface of the AgBr during this heating. Water was added, and the mixture heated for 10 minutes and filtered; HCl was added to the filtrate as long as any precipitation took place: 25 mg. of Ag were precipitated.

The experiment was repeated, the $HClO_4$ being evaporated to 0.25 cc.: not quite half of the silver was found in the filtrate.

The experiment was repeated with 100 mg. of Ag as freshly pre-

cipitated AgI. When the concentrated $HClO_4$ was added to the moist AgI, a little I_2 was liberated. While the mixture was being heated to fuming, the iodine color in the solution disappeared, but the mass of AgI remained dark in color and rapidly dissolved. After the mixture had been fumed a short time there was only a small nearly colorless residue, corresponding to 3–5 mg. of Ag as AgCl. On continuing the evaporation just to dryness, a large amount of AgCl formed. On treatment of the residue with dilute HNO_3 only one third of the silver was found in the solution.

100 mg. of Ag as AgCl were evaporated to fuming with 2 cc. of 12 n. HCl, 1 cc. of 16 n. HNO_3, and 3 cc. of 9 n. $HClO_4$; water was added and the mixture heated: the filtrate contained only an insignificant amount of chloride. 5 cc. of 9 n. $HClO_4$ were now added to the residue, and the mixture evaporated to 1.0–1.5 cc. in 2 minutes; water was added and heated: most of the AgCl was still undissolved, the filtrate containing only 3 mg. of Ag.

100 mg. of Ag as AgCl were evaporated to fuming with 5 cc. of 9 n. $HClO_4$, and kept at such a temperature so that the acid fumed gently for 10 minutes; after dilution and heating, the mixture was filtered; the filtrate contained 20 mg. of Ag.

These experiments show that the silver halides are dissolved at an increasing rate in the order AgCl, AgBr, and AgI; hence mainly on account of the oxidizing action of the hot concentrated $HClO_4$ on them.

P. 6, N. 2.—Effect of the Presence of Chloride on the Precipitation of Antimony and Tin.—300 mg. of Sb as $SbCl_3$ were evaporated to strong fuming with 5 cc. of 6 n. HNO_3 and 3 cc. of 9 n. $HClO_4$; 10 cc. of water were added, and the mixture was heated in boiling water for 10 minutes; the white precipitate was filtered off, and the filtrates saturated with H_2S: 4 mg. of Sb as Sb_2S_3 came down. This was filtered off, the H_2S boiled out of the filtrate, and 2 cc. of $AgNO_3$ solution were added: 3.5–4.0 mg. of Cl were precipitated, an amount equivalent to the antimony.

300 mg. of Sn as $SnCl_4$ were evaporated to fuming with 3 cc. of 9 n. $HClO_4$; 10 cc. of water were added, and the mixture heated as before: no precipitate was visible. $AgNO_3$ was added: a very large white precipitate separated. (This shows that moderate fuming with $HClO_4$ alone does not remove the chloride, and that then even a large quantity of tin may fail to precipitate.)

P. 6, N. 3.—Action of Fuming Perchloric Acid on Manganese, Chromium, and Vanadium.—500 mg. of Mn as $Mn(NO_3)_2$ were heated with 2 cc. of 6 n. HNO_3 and 3 cc. of 9 n. $HClO_4$ until fumes issued from the mouth of the flask; 1 cc. of 16 n. HNO_3 was added, and the mixture

again fumed: there was no precipitate. The mixture was again heated until the acid fumed more strongly: this time a large black precipitate separated. 2 cc. of fuming HNO_3 were added, and the mixture heated: the MnO_2 dissolved, but reprecipitated when the $HClO_4$ began to fume.

The experiment was repeated with 100 mg. of Mn: no precipitate came down after the first strong fuming, but a small amount separated when water was added.

This experiment was repeated, except that the $HClO_4$ was evaporated to about 0.5 cc.; the mixture was diluted and filtered, and the filtrate treated with NH_4OH and $(NH_4)_2S$: a heavy precipitate of MnS formed, it being estimated that about half the manganese had been oxidized to MnO_2.

300 mg. of Cr as $Cr(NO_3)_3$ were evaporated with 8 cc. of 6 n. HNO_3 and 3 cc. of 9 n. $HClO_4$, till the $HClO_4$ fumed moderately; 1 cc. of 16 n. HNO_3 and 2 cc. more $HClO_4$ were added, and the mixture heated to strong fuming; again 1 cc. of 16 n. HNO_3 was added, and the mixture was heated to strong fuming; then 10 cc. of water were added, and it was heated to boiling: the solution had a brown color, showing that the chromium had been partially, but not completely, oxidized to chromic acid.

The experiment was repeated with 200 mg. of Cr, except that the second fuming was continued for 5 minutes until nearly all the liquid had evaporated: during the evaporation the solution became dark-red, and red crystals (of CrO_3) separated. The residue was treated with 5 cc. of water and 1 cc. of 6 n. HNO_3: a clear dark-red solution resulted, which on gradual dilution became red and then yellowish, showing that the chromium had been almost, but not quite, completely oxidized.

To 100 mg. of V as $NaVO_3$ 1 cc. of 16 n. HNO_3 and 3 cc. of 9 n. $HClO_4$ were added, and the mixture fumed strongly for 10 minutes: an orange-red precipitate separated. The mixture was boiled with 10 cc. of water: the precipitate remained. The filtrate was treated with NH_4OH and H_2S: the color corresponded to 50 mg. of V.

The experiment was repeated with 50 mg. of V: an orange-red precipitate formed in the concentrated $HClO_4$, but this all dissolved on heating with water.

P. 6, N. 3.—Precipitation of Palladium, Gold, and Platinum by Fuming Perchloric Acid.—A solution of 50 mg. of Pd as $Pd(NO_3)_2$ in 10 cc. of 9 n. HBr was evaporated to 2 cc.; 8 cc. of 6 n. HNO_3 and 3 cc. of 9 n. $HClO_4$ were added, and the mixture evaporated to fuming; 1 cc. of 16 n. HNO_3 was added, and again the mixture was fumed, the final fuming lasting for 20 seconds; 10 cc. of water were added and the mixture heated: there was a moderate amount of fine black pre-

cipitate. This was filtered off, and the filtrate saturated with H_2S: a precipitate corresponding to 30 mg. of Pd resulted.

A solution of 50 mg. of Au as $AuCl_3$ in 8 cc. of 6 n. HNO_3 and 3 cc. of 9 n. $HClO_4$ was evaporated to fuming; 1 cc. of 16 n. HNO_3 was added, and the mixture again heated to fuming: this HNO_3 treatment was repeated, the final fuming being continued for 20 seconds; 10 cc. of water were added, and the mixture heated to boiling: there was a large dark reddish-yellow precipitate of metallic gold. This was filtered off, and the filtrate was saturated with H_2S: a precipitate of 3–4 mg. of Au as Au_2S_3 came down.

The experiment was repeated, using 50 mg. of Au as $AuBr_3$: the decomposition was more rapid than in the case of $AuCl_3$, and the precipitate at first was almost black (probably consisting of $AuBr_2$ or AuBr, since much of it dissolved on the addition of water and heating). After continued fuming, followed by dilution and filtration, 1–2 mg. of Au were precipitated from the filtrate by H_2S.

To 100 mg. of Pt as H_2PtCl_6 in a round-bottom flask 0.5 cc. of 9 n. HBr and 3 cc. of 9 n. $HClO_4$ were added, and the mixture was heated to fuming: no precipitate formed. 1 cc. of 16 n. HNO_3 was added, and the mixture was heated to fuming: there was a large dark-brown precipitate. 1 cc. more of 16 n. HNO_3 was added, and the mixture heated to fuming: the precipitate remained.

P. 6, N. 4.—Delicacy of Precipitation of Elements of the Tungsten and Tantalum Groups after Fuming with Perchloric Acid and Diluting. —The number of milligrams of the various elements shown in the first column of the following table were fumed with 3 cc. of 9 n. $HClO_4$ in a round-bottom flask (or in a platinum dish in the cases of the tantalum and columbium) till the acid distilled out of the mouth of the flask for a few seconds (or till it fumed very strongly in the dish),

Elements taken	*Precipitate*	*Treatment before fuming*
1 W as $(NH_4)_2WO_4$.....	Yellow	No HBr or HNO_3 added.
1 Sn as $SnCl_4$ in HCl....	White [a]	No HBr or HNO_3 added.
1 Sb as $SbCl_3$ in HCl....	White [b]	Evaporated with HBr, then with HNO_3 and $HClO_4$.
½ Si as Na_2SiO_3.....	None	None.
1 Si as Na_2SiO_3.....	Turbidity	None.
1 Ta as Ta_2O_5 in HF....	None	Evaporated with $HClO_4$ (no HNO_3).
2 Ta as Ta_2O_5 in HF....	White	Evaporated with $HClO_4$ (no HNO_3).
1 Cb as Cb_2O_5 in HF....	White	Evaporated with $HClO_4$ (no HNO_3).
2 Cb as solid Cb_2O_5.....	White	Evaporated with HBr, then fumed with HNO_3 and $HClO_4$.
300 Fe as $Fe(NO_3)_3$...		

[a] Separated only after diluted solution was heated for 10 minutes.
[b] About 0.3 mg. of Sb was precipitated from the filtrate by H_2S.

the fuming being preceded by the treatments shown in the last column. The solution was then diluted with 10 cc. of water and heated for 10 minutes. The character of the precipitate then formed is shown in the second column.

Valence State of Antimony after Fuming with Perchloric Acid and Boiling with Formic Acid.—To 100 mg. of Sb in HBr and Br_2 solution 3 cc. of 9 n. $HClO_4$ were added, and the mixture heated to fuming; then 1 cc. of 16 n. HNO_3 was added, and the mixture heated till the $HClO_4$ had distilled out of the flask for a few seconds; then 10 cc. of 12 n. HCO_2H were added, the solution boiled for 10 minutes and filtered; the residue was dissolved in 12 n. HCl and a drop of Br_2 solution added: it gave a yellow color, while 100 mg. of Sb as $SbCl_3$ took up 4.0 cc. of the same Br_2 solution.

Non-Precipitation of Tungstic Acid in Presence of Phosphate.—See C. E., D. 17.

Precipitation of Tungstic Acid on Evaporation with Acids in the Presence of Vanadate.—See C. E., P. 35, N. 1, last experiment.

P. 6, N. 4–6.—Behavior of Elements of the Tungsten and Tantalum Groups and Other Elements on Fuming with Perchloric Acid and Subsequent Heating with Water.—In the following tables the first column shows the number of milligrams of each element subjected to the treatment, and the second the compound of the element used. Unless otherwise stated, the solutions were evaporated to fuming in a casserole (or platinum dish when fluoride was present) with 5–8 cc. of 6 n. HNO_3 and 3 cc. of 9 n. $HClO_4$; this constituting a "single HNO_3 treatment." Then 1 cc. of 16 n. HNO_3 was added, and the mixture again evaporated to fuming. This treatment with HNO_3 was then repeated. The final fuming was carried out with the dish covered, and was continued till $HClO_4$ vapor escaped for a few seconds between the dish and cover. The mixture was then cooled, treated with 10 cc. of water, heated on a steam-bath in the covered dish for 10 minutes, and filtered hot. The third column gives the nature of the residues and the milligrams of the elements present in it. The filtrates were subjected to various tests for estimating the quantities of the elements present. The fourth column gives the results of these tests. The last column gives further information about the experiments.

Milligrams of element	*Substance taken*	*Character or content of residue*	*Found in filtrate*	*Remarks*
1 Cb 50 PO_4	Cb_2O_5 in HF Na_2HPO_4	Distinct	——	No HNO_3 added.
2 Cb 700 SO_4	Cb_2O_5 in HF H_2SO_4	Distinct	——	" " "
2 Cb 250 BO_2	Cb_2O_5 in HF HBO_2	Distinct	——	" " "
5 Cb 250 BO_2	Cb_2O_5 in HF HBO_2	Medium	1 Cb	" " "
20 Cb 250 BO_2	Cb_2O_5 in HF HBO_2	Large	5 Cb	" " "
1 Cb 10 Ti	Cb_2O_5 in HF TiO_3H_2 in HCl	Distinct	——	
2 Ta 50 PO_4	Ta_2O_5 in HF Na_2HPO_4	Distinct	——	No HNO_3 added.
2 Ta 700 SO_4	Ta_2O_5 in HF H_2SO_4	Distinct	——	" " "
5 Ta 250 BO_2	Ta_2O_5 in HF HBO_2	None	——	" " "
10 Ta 250 BO_2	Ta_2O_5 in HF HBO_2	None	——	" " "
50 Ta 250 BO_2	Ta_2O_5 in HF HBO_2	Medium	35–40 Ta	" " "
10 Ti	TiO_3H_2 in HCl	None	10 Ti	One HNO_3 treatment.
20 Ti	TiO_3H_2 in HCl	Slight turbidity	20 Ti	" " "
25 Ti	TiO_3H_2 in HCl	Medium	20 Ti	" " "
20 Ti	TiO_2 in HF	Slight turbidity	20 Ti	" " "
25 Ti	TiO_2 in HF	Medium	20 Ti	" " "
10 Ti 3 Ta	TiO_3H_2 in HCl Ta_2O_5 in HF	None	10 Ti 3 Ta	
10 Ti 5 Ta	TiO_3H_2 in HCl Ta_2O_5 in HF	None	10 Ti 5 Ta	
10 Ti 10 Ta	TiO_3H_2 in HCl Ta_2O_5 in HF	Heavy white[a]	——	
20 Ti 10 Ta	TiO_3H_2 in HCl Ta_2O_5 in HF	Heavy white	——	
20 Ti 5 Ta	TiO_2 in HF Ta_2O_5 in HF	White[b]	20 Ti 5 Ta	
20 Ti 10 Ta	TiO_2 in HF Ta_2O_5 in HF	1 Ti 4 Ta	19 Ti 6 Ta	
50 Ti 3 Ta	TiO_2 in HF Ta_2O_5 in HF	20 Ti 1 Ta	30 Ti 2 Ta	
100 Sb	$SbCl_3$ in HCl	Large Sb	1 Sb	First treated with HBr and Br_2.
500 Sb	Sb_2O_3	Large Sb	1 Sb	First treated with HBr and Br_2.

[a] Some Ta and some Ti were both present in the residue.
[b] Dissolved in hot water on 20 minutes' heating.

Milligrams of element	*Substance taken*	*Character or content of residue*	*Found in filtrate*	*Remarks*
1 Sb 750 SO_4	$SbCl_3$ in HCl Na_2SO_4	None	1 Sb	
3 Sb 750 SO_4	$SbCl_3$ in HCl Na_2SO_4	2 Sb	1 Sb	
5 Sb 150 BO_2	$SbCl_3$ in HCl HBO_2	4 Sb	1 Sb	
500 Sb 150 BO_2	Sb_2O_3 HBO_2	Large	1½ Sb	First with HBr-Br_2.
1 Sb 100 PO_4	$SbCl_3$ in HCl Na_2HPO_4	None	1 Sb	
3 Sb 100 PO_4	$SbCl_3$ in HCl Na_2HPO_4	2 Sb	1 Sb	
500 Sn	$SnCl_4$ in HCl	Large Sn	0 Sn	See Note *c*.
1 Sn 100 PO_4	$SnCl_4$ in HCl Na_2HPO_4	1 Sn	0 Sn	
1 Sn 150 BO_2	$SnCl_4$ in HCl HBO_2	1 Sn	0 Sn	
1 Sn 750 SO_4	$SnCl_4$ in HCl H_2SO_4	1 Sn	0 Sn	
1 W 750 SO_4	$(NH_4)_2WO_4$ H_2SO_4	Yellow	——	No HNO_3 added.
1W 150 BO_2	$(NH_4)_2WO_4$ HBO_2	Yellow	——	No. HNO_3 added.
3 Mo	$(NH_4)_2MoO_4$	Faint turbidity	3 Mo	No HNO_3 added.
5 Mo	$(NH_4)_2MoO_4$	2 Mo	3 Mo	" " "
10 Mo	$(NH_4)_2MoO_4$	7 Mo	3 Mo	" " "
15 Mo	$(NH_4)_2MoO_4$	12 Mo	3 Mo	" " "
20 Mo	$(NH_4)_2MoO_4$	17 Mo	3 Mo	" " "
500 Mo 100 PO_4	MoO_3 H_3PO_4	Small yellow	Large Mo	
100 Si	Na_2SiO_3	100 Si	0 Si	
100 Fe	$Fe_2(SO_4)_3$	None	100 Fe	No HNO_3 added.
100 Cr	$Cr_2(SO_4)_3$[d]	Large	Trace Cr	No HNO_3 added; only once fumed.
100 Bi	$Bi_2(SO_4)_3$	Medium	60 Bi	No HNO_3 added.
50 V	Na_3VO_4	None	50 V	" " "
100 V 500 Sn	Na_3VO_4 $SnCl_4$ in HCl	Yellow	35 V 20 Sn[c]	One HNO_3 treatment.
100 V 500 Sn	Na_3VO_4 $SnBr_4$ in HBr	Large yellow	16 V 0 Sn	
10 V 500 Sn	Na_3VO_4 $SnBr_4$ in HBr	Large yellow	0 V 0 Sn	
200 Zr	$Zr(NO_3)_4$	None	200 Zr	
500 Zr	$Zr(NO_3)_4$	None	500 Zr	

[c] In several experiments with $SnCl_4$, in which the mixture was heated to fuming with $HClO_4$ alone, or once just to fuming with $HClO_4$ and HNO_3, the filtrate was found to contain both tin and chloride (see C. E., P. 6, N. 2).

Milligrams of element	*Substance taken*	*Character or content of residue*	*Found in filtrate*	*Remarks*
100 Zr 50 Ti	$Zr(NO_3)_4$ TiO_3H_2 in HCl	None	100 Zr 50 Ti	
100 Zr 75 Ti	$Zr(NO_3)_4$ TiO_3H_2 in HCl	None	100 Zr 75 Ti	
100 Zr 100 Ti	$Zr(NO_3)_4$ TiO_3H_2 in HCl	Turbid when hot 4 Ti when cool	——	Residue not analyzed.
100 V	Na_3VO_4	Yellow, 50V	50 V	See note *e*.
100 Ti 5 V	TiO_3H_2 in HCl Na_3VO_4	White, 85 Ti 4.9 V	15 Ti 0.1 V	" " "
100 Zr 5 V	$Zr(NO_3)_4$ Na_3VO_4	Yellow, med. Zr 3 V	Large Zr 2 V	" " "
100 V 10 Ti	Na_3VO_4 TiO_3H_2 in HCl	Yellow, 86 V 0 Ti	14 V 10 Ti	" " "
100 Ti 5 V	TiO_3H_2 in HCl Na_3VO_4	Yellow, small Ti 4 V	Large Ti 1 V	See note *e*.
100 Zr 5 V	$Zr(NO_3)_2$ Na_3VO_4	White, small Zr 2.5 V	Large Zr 2.5 V	" " "
100 V 10 Ti	Na_3VO_4 TiO_3H_2 in HCl	Yellow, 92 V 0 Ti	8 V 10 Ti	" " "
100 Rh	$RhCl_3$ in HCl	None	100 Rh	
100 Te	TeO_2 in HCl	None	100 Te	
100 Te 300 Sn	TeO_2 in HCl $SnCl_4$ in HCl	Large	6 Te 0 Sn	
100 Th 80 PO_4	$Th(NO_3)_4$	Thick gel	0 Th 20 PO_4	No HNO_3 added.
300 Sn 5 Pb	$SnCl_4$ in HCl $Pb(NO_3)_2$	Large Sn Trace Pb	0 Sn 5 Pb	
9 Pb 200 Cr	$Pb(NO_3)_2$ CrO_3	1 Pb	8 Pb[f]	No HNO_3 added.
300 Pb	$PbSO_4$	285 Pb	15 Pb[g]	No HNO_3 added; fumed in flask.
200 Ca	$CaSO_4$	165 Ca	35 Ca[h]	No HNO_3 added; fumed in flask.
525 K	KCl	225 K[i]	300 K[k]	No HNO_3 added.

[d] Prepared by evaporating $Cr(NO_3)_3$ solution to dryness with H_2SO_4.

[e] In these experiments the substances were digested on a steam-bath for 15 minutes with 10 cc. of 27 n. HF. Then 8 cc. of 6 n. HNO_3 and 3 cc. of 9 n. $HClO_4$ were added, and the mixture evaporated to fuming. 1 cc. of 16 n. HNO_3 was added, and the mixture again fumed. 1 cc. of 16 n. HNO_3 was again added, and the mixture evaporated to strong fuming. A cover was then put on the dish, and the flame of the burner was so regulated that the $HClO_4$ fumed moderately for 15 minutes; more $HClO_4$ being added from time to time to keep the volume nearly 2 cc. Then 10 cc. of water were added, the mixture was heated, and the residues, if any, were filtered off.

[f] Of this, 5 mg. of Pb precipitated as $PbCrO_4$ on cooling.

[g] Of this, 1 to 2 mg. of Pb precipitated as $PbSO_4$ on cooling.

[h] Of this, 5 mg. precipitated as $CaSO_4$ on cooling.

[i] This dissolved in 5 cc. of boiling water.

[k] Of these 300 mg., at least 250 mg. separated as $KClO_4$ on cooling.

P. 6, N. 4–6.—Behavior of Elements of the Tungsten and Tantalum Groups and of Related Elements on Fuming with Perchloric Acid and Subsequent Boiling with Formic Acid.—The substances shown in the first column of the following tables were heated in a 50-cc. round-bottom flask first with HBr and Br_2 (except in cases indicated by a suffix *a*) and 3 cc. of 9 n. $HClO_4$ till the $HClO_4$ began to fume; then 1 cc. of 16 n. HNO_3 was added, and the mixture was heated till the neck of the flask was filled with a column of $HClO_4$ vapor and the $HClO_4$ had distilled out of the mouth of the flask for a few seconds. The mixture was then cooled, diluted with 10 cc. of 12 n. $HCHO_2$, and boiled with a reflux-cooler for 15 minutes. The mixture was then filtered boiling-hot, yielding the "first precipitate"; and the filtrate was evaporated in a 50-cc. flask till the $HClO_4$ began to fume. The mixture was cooled, treated with 1 cc. of 16 n. HNO_3, and heated to strong fuming, in the same way as before. The mixture was diluted with 10 cc. of water, heated to boiling, and filtered. The amount of this "second precipitate" was estimated from its appearance, and the filtrate was tested in the way shown in the last column of the tables. The way in which the element divided itself is shown in the third, fourth, and fifth columns.

In the series of titanium experiments recorded below the dotted line in the second table no HBr, Br_2, or HNO_3 was added, 5 cc. of 9 n. $HClO_4$ (instead of 3 cc.) were used, and this was boiled off in a 50-cc. flask, till 3 cc. remained (not merely till $HClO_4$ began to boil out of the flask).

Milligrams of element	*Substance taken*	*1st precipitate*	*2d precipitate*	*Filtrate*	*Method of testing*
1 W	$(NH_4)_2WO_4$[a]	1 W	0 W	0 W	Filtrate with $SnCl_2$.
100 W	$(NH_4)_2WO_4$[a]	Large W	0.3 W	—	Appearance of precipitate.
2 Sn	$SnCl_4$ in HCl	2 Sn	0 Sn	0 Sn	Filtrate with H_2S.
500 Sn	$SnCl_4$ in HCl	500 Sn	0 Sn	0 Sn	" " "
2 Sb	$SbCl_3$ in HCl	1.9 Sb	0 Sb	0.1 Sb	" " "
100 Sb	$SbCl_3$ in HCl	Large Sb	0 Sb	0.8 Sb	" " "
500 Sb	$SbCl_3$ in HCl	Large Sb	0 Sb	1 Sb	" " "
10 Cb	Cb_2O_5 in HF[a]	Medium Cb	0 Cb[b]	—	— —
2 Ta	Ta_2O_5 in HF[a]	Small Ta	0 Ta[b]	—	— —
5 Mo	$(NH_4)_2MoO_4$	3.5 Mo	.01 Mo	1.5 Mo	With H_2S on steam-bath 15 min.
100 Mo	$(NH_4)_2MoO_4$	98.8 Mo	.2 Mo	1 Mo	With H_2S on steam-bath 15 min.
25 V	$(NH_4)_3VO_4$	0 V	Not tried	25 V	Shown by absence of a precipitate.
100 V	$(NH_4)_3VO_4$	10 V^V	" "	90 V^{IV}	Appearance of precipitate.
500 Sn 80 V	$SnCl_4$ in HCl $(NH_4)_3VO_4$	Large Sn[c] 8 V	" "	0.5 Sn 72 V	Filtrate with H_2S. Precipitate with H_2O_2 after dissolving.
500 Sn 5 V	$SnCl_4$ in HCl $(NH_4)_3VO_4$	499 Sn 4 V	" "	1 Sn 1 V	Filtrate with H_2S. Filtrate with H_2O_2.
500 Pb	$PbSO_4$	Large $PbSO_4$	" "	18 Pb[d]	With H_2S after fuming out the acid.
400 Sb 200 Bi	$SbCl_3$ in HCl $Bi(NO_3)_3$	Large[e]	" "	0 Sb 0 Bi	With H_2S after partial neutralization.
15 Ti	TiO_2 in HF[a]	11Ti	Not tried	4 Ti	Filtrate with NH_4OH.
15 Ti	$TiBr_4$ in HCl[a]	11½ Ti	0	3½ Ti	Filtrate with NH_4OH.

[a] The first heating with HBr and Br_2 was omitted.

[b] This conclusion is based not on direct experiment made as in the other cases, but on the fact that the same amount of precipitate resulted in two independent experiments in which $HCHO_2$ and water, respectively, were used for the dilution.

[c] The residue was yellow before the $HCHO_2$ boiling, gray after it.

[d] This remained in solution on cooling.

[e] The precipitate ran through the filter when washed with water, but not when washed with 0.3–1.0 n. $HClO_4$.

Milligrams of element	*Substance taken*	*1st precipitate*	*2d precipitate*	*Filtrate*	*Filtrate tested with*
15 Ti[j]	$TiBr_4$ in HCl[a]	12 Ti	Not tried	3 Ti	NH_4OH.
5 Ti[j]	$TiBr_4$ in HCl[a]	1 Ti[f]	" "	4 Ti	NH_4OH.
50 Ti	$TiBr_4$ in HCl[a]	—	" "	2 Ti[g]	NH_4OH.
100 Ti 300 PO_4	TiO_2 in HF H_3PO_4	Large	" "	0 Ti 20 PO_4	H_2O_2. $(NH_4)_2MoO_4$.
100 Zr 200 PO_4	$ZrO(NO_3)_2$ H_3PO_4	Large	" "	0 Zr 0 PO_4	NH_4OH. $(NH_4)_2MoO_4$.
100 Zr 300 PO_4	$ZrO(NO_3)_2$ H_3PO_4	Large	" "	0.7 Zr 10 PO_4	NH_4OH. $(NH_4)_2MoO_4$.
10 Ti	TiO_3H_2 in HCl	6 Ti[nh]	Not tried	4 Ti	NH_4OH.
5 Ti	"	1 Ti[n]	" "	4 Ti	NH_4OH.
5 Ti	"	1 Ti[n]	" "	4 Ti	NH_4OH.
3 Ti	"	0 Ti	" "	3 Ti	NH_4OH.
5 Ti[k]	"	1 Ti[n]	" "	4 Ti	NH_4OH.
10 Ti[l]	"	6 Ti[n]	" "	4 Ti	NH_4OH.
5 Ti[l]	"	1 Ti[n]	" "	4 Ti	NH_4OH.
3 Ti[l]	"	0 Ti	" "	3 Ti	NH_4OH.
5 Ti[m]	"	< 1 Ti[n]	" "	> 4 Ti	NH_4OH.
10 Ti[m]	"	$5\frac{1}{2}$ Ti[n]	" "	$4\frac{1}{2}$ Ti	NH_4OH.

[f] The solution became turbid only after about 5 minutes' heating with $HCHO_2$, and the turbidity was distinct after 10 minutes, while in the experiments with 15 mg. of Ti the precipitate formed on strong fuming with $HClO_4$ alone, or with $HClO_4$ and HNO_3.

[g] Owing to severe bumping during the refluxing with $HCHO_2$, nearly one third of the mixture was lost.

[h] As to the modification of the fuming process used in these experiments, see the statement on page 305 just preceding these tables.

[j] These experiments were repeated except that the fumed mixture was boiled with 10 cc. of 22 n. $HCHO_2$ (instead of with 12 n.): the results were almost exactly the same.

[k] In this experiment the $HCHO_2$ mixture was refluxed for 60 minutes (instead of 15 minutes).

[l] These experiments differed from the five preceding ones only in that 16 n. HNO_3 was added with the $HClO_4$ before the fuming.

[m] In these experiments the $HClO_4$ after fuming was diluted with 10 cc. of water (instead of with 10 cc. of 12 n. $HCHO_2$).

[n] In all these 5-mg. experiments, the hot $HClO_4$ mixture was clear, but a milk-white turbidity formed on cooling; this dissolved on adding $HCHO_2$, but not completely on adding water; and a precipitate began to separate from the clear $HCHO_2$ solution after 2–4 minutes' boiling, and increased for 5–7 minutes. In the 10-mg. experiments some precipitate separated from the hot fuming acid, increased on cooling, dissolved only partially on diluting with $HCHO_2$ or water, and increased gradually during the 10 minutes' boiling.

The results with titanium given in the two preceding tables clearly show that 3–4 mg. of this element remain in solution, whatever the amount present (at any rate up to 15 mg.). The fact that in the earlier experiments (recorded in the tables on pages 302–304) made in casseroles or platinum dishes 20 mg. remained in solution is doubtless due to the much milder fuming of the $HClO_4$ in those experiments. (Thus in two later experiments in which 10 mg. were heated in a covered casserole, the whole remained in solution in one case where the mixture was heated only to moderate fuming, and about 1 mg. precipitated in the other case where the fuming was continued till dense fumes began to escape between the dish and cover.) That different results were obtained by the two methods was discovered by R. D. Fowler.

Non-Effect of Boric Acid on Precipitation of Elements of the Tungsten and Tantalum Groups after Evaporating with Hydrofluoric Acid.—To solutions of 1 mg. of W, 1 mg. of Cb, 1 mg. of Ta, 1 mg. of Sn, and 20 mg. of Sb, in separate experiments, in 3 cc. or 5 cc. of 27 n. HF were added 250 mg. of H_3BO_3 and 5 cc. of 16 n. HNO_3; the solutions were evaporated to dryness and the residues treated with 6 n. HNO_3, which was then diluted with water: in each case a small residue of the oxide remained. (This shows that the boron was volatilized by the HF, as may be seen by comparing the results with those in the experiments with HBO_2 in the tables on pages 302 and 303. See also C. E., P. 3, N. 4.)

To the mixtures were added 500 mg. more H_3BO_3: the residues did not dissolve (indicating that to make them soluble they must be fumed with $HClO_4$ in the presence of H_3BO_3).

P. 6, N. 7, 8.—Behavior of the Gold-Group and Other Reducible Elements on Fuming with Perchloric Acid and Subsequent Heating with Formic Acid.—The substances shown in the second column of the following tables were heated in a 50-cc. round-bottom flask first with HBr and Br_2 (except when an *a* is suffixed) and 3 cc. of 9 n. $HClO_4$ till the $HClO_4$ began to fume; then 1 cc. of 16 n. HNO_3 was added, and the mixture was heated till the flask became filled with a column of $HClO_4$ vapor, and the $HClO_4$ had distilled out of the mouth of the flask for a few seconds. The mixture was then cooled, diluted with 10 cc. of 12 n. $HCHO_2$, and heated for the time shown in the fifth column. The mixture was then filtered, and the filtrate, unless otherwise stated, was tested in the way shown in the last column, with the results shown in the third and fourth columns.

Milligrams of element	*Substance taken*	*Found in*		*Minutes boiled*	*Method of testing* (filtrate unless otherwise stated)
		precipitate	*filtrate*		
1 Au	$AuCl_3$	1 Au	0 Au	15	With H_2O_2 and NaOH.
10 Au	$AuCl_3$	9.7 Au	0.3 Au	10	" " " "
100 Au	$AuCl_3$	100 Au	0 Au	15	" " " "
1 Pt	$PtCl_4$	1 Pt	0 Pt	15	With H_2S at 90°.
10 Pt	$PtCl_4$	9.7 Pt	0.3 Pt	15	With H_2S at 90°.
100 Pt	$PtBr_4$	99.8 Pt	0.2 Pt	15	With H_2S at 90°.
2 Pd	$PdCl_2$	1.9 Pd	0.1 Pd	5	With H_2S.
80 Pd	$PdCl_2$[a]	75 Pd	5 Pd	30	" "
70 Pd	$PdCl_2$[a]	66 Pd	4 Pd	30	" "
85 Pd	$PdBr_2$	85 Pd	0 Pd	15	" "
1 Hg	$Hg(ClO_4)_2$	1 Hg	0 Hg^{I} 0 Hg^{II}	15	With NH_4Cl (for Hg^{I}). With H_2S (for Hg^{II}).
5 Hg	$HgCl_2$	4.5 Hg	0.5 Hg	15	With H_2S.
300 Hg	$HgBr_2$	300 Hg[b]	0 Hg^{I} 0 Hg^{II}	15	With NH_4Cl (for Hg^{I}). With H_2S (for Hg^{II}).
500 Hg	$Hg_2(NO_3)_2$[a]	500 Hg	0 Hg	15	With H_2S.
100 Ag	$AgNO_3$[a]	1 Ag	99 Ag	15	Dissolving precipitate, adding NaCl.
100 Ag	AgBr	50 Ag[b]	50 Ag	15	With NH_4Cl.
2 Ag	AgBr	1 Ag[b]	1 Ag	15	With NH_4Br.
500 Cu	$Cu(NO_3)_2$	0 Cu	500 Cu	15	Absence of precipitate.
500 Bi	$Bi(NO_3)_3$	0 Bi	500 Bi	15	" " "
5 Ir	$IrCl_4$[a]	0 Ir	5 Ir	Note *c*	" " "
10 Ir	$IrCl_4$[a]	0 Ir	10 Ir	15	" " "
10 Ir	$IrCl_4$[a]	0 Ir	10 Ir	30[d]	" " "
10 Ir	$IrCl_4$[a]	0.1 Ir	9.9 Ir	15[d]	Trace of precipitate.
10 Ir	$IrCl_4$[a]	0 Ir[e] 0.01 Ir[e]	10 Ir 10 Ir	15 15	Absence of precipitate. Trace of precipitate.
50 Ir	$IrCl_4$[a]	0 Ir	50 Ir	15	Absence of precipitate.
100 Ir	$IrCl_4$[a]	10 Ir[f] 0.5[f] 1.5[f] 10[f]	90 Ir 89.5 88 78	15 15 15 15	Looks of precipitate. " " " " " " Weighing precipitate.
5 Ir 50 Pt	$IrCl_4$[a] $PtCl_4$	4 Ir 50 Pt	1 Ir 0 Pt	15	With H_2S.
5 Ir 5 Rh 50 Pt	$IrCl_4$[a] $RhCl_3$ $PtCl_4$	8 { Ir Rh 50 Pt	2 { Ir Rh 0 Pt	15	With H_2S.

a-f For the meaning of these signs see the foot-notes on the next page.

Milligrams of element	*Substance taken*	*Found in*		*Minutes boiled*	*Method of testing* (filtrate unless otherwise stated)
		precipitate	*filtrate*		
1 Rh	$RhCl_3$	0 Rh	1 Rh	15	No precipitate on filter.
10 Rh	$RhCl_3$	0.8 Rh	9.2 Rh	15	Looks of precipitate.
10 Rh	$RhCl_3$	1.7 Rh	8.3 Rh	30	Weighing precipitate.
70 Rh	$RhCl_3$[a, g]	17 Rh	53 Rh	15	Weighing precipitate.
100 Te	$TeCl_4$	0 Te	100 Te	15	
1 Tl	$TlNO_3$	0 Tl	1 Tl^{I} 0 Tl^{III}	15	With NH_4Br followed by SO_2.
100 Tl	$TlNO_3$	0 Tl	100 Tl^{I} 0 Tl^{III}	15	With NaBr followed by SO_2.
100 Fe	$Fe(NO_3)_3$[a]	0 Fe	70 Fe^{II} 30 Fe^{III}	15	Color with KSCN.
500 Fe	$Fe(NO_3)_3$[a]	0 Fe	340 Fe^{II} 160 Fe^{III}	15	" " "
250 Cr	K_2CrO_4[a]	0 Cr	250 Cr^{III} 0 Cr^{VI}	15	With $BaCl_2$ after neutralization.
50 Se	SeO_2[a]	0 Se	50 Se	15	With HCl and SO_2.
50 Se	SeO_2[h]	0 Se	50 Se	15	" " " "
50 Se 5 Pd	SeO_2[a] $Pd(ClO_4)_2$	0 Se 5 Pd	50 Se 0 Pd	15	" " " "
500 Mn	$Mn(NO_3)_2$[i]	0 Mn	500 Mn	2	

[a] No HBr or Br_2 was added in these cases.

[b] Partly as metal, partly as bromide.

[c] The $HCHO_2$ solution was heated to 60–70° for 20 minutes: the deep-purple solution became bluish-green. The solution was then heated to 100° (in a boiling water-bath) for 1 hour: the solution became very pale olive-green, and no precipitate separated.

[d] The mixture was heated at 80–90° before the 15-minute boiling. It became pale olive-green, and in this preliminary heating no precipitate formed.

[e] These are the quantities precipitated in two successive 15-minute boilings.

[f] These figures show the quantities precipitated in four successive 15-minute boilings with $HCHO_2$. After the second boiling, the olive-green filtrate was evaporated to slight fuming, and a fresh 10-cc. portion of 12 n. $HCHO_2$ was added. After the third boiling, the filtrate was evaporated to slight fuming, 1 cc. of 16 n. HNO_3 was added, and the mixture strongly fumed. The solution was dark-red after fuming with HNO_3 and adding $HCHO_2$; but became olive-green after boiling.

[g] In this experiment nearly the same quantity of metal precipitated, as judged by its appearance, in three successive boilings with $HCHO_2$, even when the mixture was fumed with addition of HNO_3 in between.

[h] No HBr, Br_2, or HNO_3 was added, and the solution was not heated before the $HCHO_2$ was added.

[i] In the fuming with $HClO_4$ and HNO_3 about 50 mg. of Mn separated as MnO_2. With $HCHO_2$ in the cold there was no apparent action in 2 minutes; but the MnO_2 was rapidly reduced when the mixture was boiled.

P. 6, N. 10.—Effect of Dilute Formic Acid on the Reduction of Mercury and Thallium.—The substances in the second column of the following table were mixed in a 50-cc. round-bottom flask with 3 cc. of 9 n. $HClO_4$, 1 cc. of 7 n. HBr, and 5 drops of Br_2; and the mixture was heated to fuming. Then 1 cc. of 16 n. HNO_3 was added, and the solution heated as before until the flask was filled with $HClO_4$ vapor. The solution was cooled, 10 cc. of 6 n. $HCHO_2$ were added, and the solution heated as shown in the fifth column. The precipitate was filtered out; and the filtrate was tested in the way shown in the last column, with the results shown in the third and fourth columns. The mercury precipitates consisted partly of the metal and partly of Hg_2Br_2.

Milligrams of element	*Substance taken*	*Present in*		*Way of heating*	*Filtrate tested with*
		precipitate	*filtrate*		
1 Hg	$Hg(ClO_4)_2$	0 Hg	0.9 Hg^{II} 0.1 Hg^{I}	Steam-bath, 10 min.	NH_4Cl.
200 Hg	$Hg(ClO_4)_2$	Medium Hg	0 Hg^{II} Large Hg^{I}	Steam-bath, 10 min.	NH_4Cl; then H_2S.
500 Hg	$Hg(ClO_4)_2$	Large Hg	0.5 Hg^{II} Large Hg^{I}	Steam-bath, 10 min.	NH_4Cl; then H_2S.
50 Tl	TlCl	0 Tl	0 Tl^{III} 50 Tl^{I}	Boiled 15 min.	NH_4Br, then H_2SO_3.

Effect of Perchloric Acid Concentration on the Reduction of Mercury.—5 mg. of Hg as $Hg(ClO_4)_2$, dissolved in one case in 1 cc. of 9 n. $HClO_4$, and in another case in 4 cc. of this acid, were refluxed for 15 minutes with 10 cc. of 12 n. $HCHO_2$; the solutions were filtered, and the filtrates were tested with H_2S: in the first case no mercury was found, in the second an amount less than 0.05 mg.

P. 6, N. 12.—Precipitation of Potassium Perchlorate and of Calcium Sulfate on Cooling the Perchloric-Acid–Formic-Acid Solution.—See the last experiments in the table on page 304.

50 mg. of K as KNO_3 were heated to strong fuming with 3 cc. of 9 n. $HClO_4$; 10 cc. of 12 n. $HCHO_2$ were added, and the mixture was heated to boiling and then cooled: a white crystalline precipitate corresponding to 20–30 mg. of K separated on cooling. 2 cc. of 2 n. bromine-free HBr were added, and the mixture was shaken under a water tap: the precipitate still remained. The mixture was then filtered, and the precipitate was washed slowly and carefully with 10 cc. of 1 n. bromine-free HBr solution: about one third of the precipitate remained undissolved on the filter.

500 mg. of Ca as freshly precipitated $CaSO_4$ were boiled 15 minutes

with 3 cc. of 9 n. $HClO_4$ and 10 cc. of 12 n. $HCHO_2$, the large precipitate was filtered out, and the filtrate cooled: a white precipitate of about 0.5 mg. of Ca came down. The solution was then evaporated to 9 cc. and cooled: a white precipitate of 1–2 mg. of Ca separated. 1 cc. of 6 n. NH_4Br was then added: the precipitate did not increase in size. The mixture was then diluted to 17 cc., heated till the precipitate disappeared, and cooled: no precipitate resulted.

P. 7, N. 3.—Solution of the Oxides of the Tungsten and Tantalum Groups in Hydrofluoric Acid.—500 mg. of Sn as metal, of Sb as metal, of W as Na_2WO_4, of Ti as TiO_2, of Mo as MoO_3, of Te as TeO_2, and 30 mg. of Ge as GeO_2, in separate experiments, were treated with HNO_3, the liquid evaporated off, and the residue heated at 120° for at least an hour; the residue was then heated on a steam-bath for 5 minutes with 5–10 cc. of 27 n. HF: a clear or slightly opalescent solution resulted in every case except that of tin. Then 20 cc. of cold water were added to each solution: the tin solution became clear, and all the others remained so.

To an HF solution of 500 mg. of Sn as H_2SnO_3, 400 mg. of PO_4 as Na_2HPO_4 were added, the mixture evaporated to dryness three times with HNO_3, and the residue heated an hour at 120°; then it was heated with 5 cc. of 27 n. HF, and finally 20 cc. of water were added: a large residue of at least 100 mg. of Sn remained, and this did not dissolve on a second treatment with HF and water.

To 500 mg. of Sn as metal dissolved in 5 cc. of 9 n. HBr, 400 mg. of PO_4 as Na_2HPO_4 were added, then 3 cc. of Br_2; the mixture was evaporated to 1 cc.; then 5 cc. of 6 n. HNO_3 and 2 cc. of 9 n. $HClO_4$ were added, and the mixture was evaporated to fuming; 1 cc. of 16 n. HNO_3 and 2 cc. of 9 n. $HClO_4$ were added, and the mixture evaporated to strong fuming; 10 cc. of water were added, and the mixture heated and filtered: the solution contained 3 mg. of Sn. The large white residue was digested with 10 cc. of 27 n. HF: it all dissolved. Then H_2SO_4 was added, and the mixture evaporated to fuming: the precipitate again separated.

Three portions of 500 mg. of Sn as metal were treated with three portions of 5 cc. of 16 n. HNO_3, to one of which had been added 500 mg. of V as Na_3VO_4, to another 500 mg. of W as Na_2WO_4, and to the third 500 mg. of Mo as $(NH_4)_2MoO_4$; and the mixtures were evaporated to dryness, and heated at 120° for one hour; the residues were then treated with 5–10 cc. of 27 n. HF and with 25 cc. of water: the vanadium-tin mixture dissolved completely in 10 cc. of cold concentrated HF; the tungsten-tin mixture dissolved in 5 cc. of HF after dilution with 25 cc. of water; and the molybdenum-tin mixture dissolved in 10 cc. of HF after dilution with 80 cc. of water.

P. 7, N. 4.—Behavior of Lead Sulfate and of Calcium Sulfate with Hydrofluoric Acid.—About 100 mg. of Pb as $PbSO_4$ were digested with 10 cc. of 27 n. HF, the mixture was filtered after the addition of 25 cc. of cold water, and the filtrate tested for lead: it contained 15 mg. of Pb. The residue was treated with 5 cc. of 12 n. HCl and the mixture evaporated just to dryness, this being repeated five times; then 10 cc. of hot water were added: the solid dissolved, showing that the $PbSO_4$ had been largely or wholly converted into PbF_2 by the HF.

100 mg. of Pb as precipitated $PbSO_4$ were digested with 8 cc. of 27 n. HF for 4 minutes on a steam-bath; the mixture was cooled, diluted with 20 cc. of water, and filtered: the filtrate contained 10–12 mg. of Pb. To the residue were added 5 cc. of 12 n. HCl and 0.5 cc. of 16 n. HNO_3, and the mixture was evaporated almost to dryness; 2 cc. of 12 n. HCl were added, and the mixture was evaporated to 0.3 cc.; 5 cc. of water were added, and the cold mixture was filtered, and the filtrate treated with H_2S: it contained 3 mg. of Pb. The residue was washed by pouring a cold 10-cc. portion of 0.6 n. HCl repeatedly through the filter: the solution was found to contain 15–20 mg. of Pb. This washing was repeated twice: each time the solution contained 15–20 mg. of Pb, showing that the residue on the filter was mainly $PbCl_2$ (since only about 5 mg. of Pb would have been extracted if the residue had been $PbSO_4$). The remaining residue was dissolved in hot 3 n. $NH_4C_2H_3O_2$, the solution treated with H_2S, and filtered: a precipitate of PbS corresponding to 35–40 mg. of Pb resulted. This was filtered off, and 2 cc. of 1 n. $BaCl_2$ added: a small white precipitate estimated to contain 3 mg. of SO_4 formed.

500 mg. of $CaSO_4 \cdot 2H_2O$ were treated for 10 minutes in a platinum dish on a steam-bath with 10 cc. of 27 n. HF. The mixture was filtered, the gelatinous precipitate was heated with HNO_3, and then (after evaporation) with HNO_3 and HCl; the mixture was evaporated, and 5 cc. of water were added: the residue entirely dissolved (showing that the $CaSO_4$ was converted into CaF_2, and that the CaF_2 was entirely decomposed by the two evaporations with acid).

See also C. E., P. 3, N. 2, as to the solubility of fluorides in HF.

P. 7, N. 4.—Behavior of a Mixture of Bismuth and Antimony Oxides with Hydrofluoric Acid.—A mixture of 200 mg. of Bi and 400 mg. of Sb as oxides, precipitated by fuming with $HClO_4$ (in C. E. on page 306), was digested with 10 cc. of 27 n. HF for 5 minutes on a steam-bath, cooled, diluted with 25 cc. of water, and filtered. The HF filtrate was evaporated to fuming with 1 cc. of 36 n. H_2SO_4, diluted, and treated with 5 cc. of Na_2S reagent: there formed a black precipitate (of Bi_2S_3) corresponding to 2–3 mg. of Bi, showing that this amount had dissolved in the HF. The Na_2S solution was acidified:

a very large orange-yellow precipitate of Sb_2S_3 separated. The residue from the HF treatment was washed with 1 n. $HClO_4$ (since water caused it to pass through the filter), and dissolved in acids, and the solution tested: 40–50 mg. of Sb and a large amount of bismuth were found present.

P. 7, N. 4.—Behavior of Thorium Phosphate with Hydrofluoric Acid.—100 mg. of Th as thorium phosphate, which had been fumed with $HClO_4$, diluted, and filtered, and was in the form of a gelatinous precipitate, were digested with 8 cc. of 27 n. HF; the mixture was cooled, treated with 20 cc. of water, and filtered; the filtrate was evaporated to fuming with H_2SO_4, cooled, and diluted; portions were tested for PO_4, and for thorium with NH_4OH: it contained about 15 mg. of PO_4, and only an insignificant quantity of thorium.—The experiment was repeated: no Th and 20 mg. of PO_4 were found in the HF solution.

P. 8, N. 1.—Action of Sodium Carbonate Solution on Calcium Fluoride.—1 g. of $CaSO_4 \cdot 2H_2O$ was heated with 10 cc. of 27 n. HF on a steam-bath, 25 cc. of water were added, and the precipitate was filtered out, washed, and boiled for 15 minutes, in a flask with a reflux tube, with 50 cc. of 3 n. Na_2CO_3 in which 10 g. more of solid Na_2CO_3 were dissolved; the mixture was filtered, and the filtrate acidified and treated with $BaCl_2$: no precipitate formed, showing that the $CaSO_4$ had been completely converted to CaF_2. Through the residue on the filter was poured repeatedly a 10-cc. portion of 3 n. $HClO_4$; a small gelatinous residue remained. The $HClO_4$ solution was treated with NH_4OH and $(NH_4)_2C_2O_4$: NH_4OH produced a small gelatinous precipitate (of 5–10 mg. of CaF_2), and $(NH_4)_2C_2O_4$ a large white precipitate. The residue from the $HClO_4$ treatment was boiled with 12 n. HCl, the solution diluted, filtered, and treated with NH_4OH and $(NH_4)_2C_2O_4$: NH_4OH produced a small gelatinous precipitate (of CaF_2), and $(NH_4)_2C_2O_4$ an additional one, its size indicating that all but 10 mg. of the calcium dissolved in the $HClO_4$.

P. 8, N. 2.—Action of Sodium Carbonate Solution on Barium Sulfate and on Chromic Sulfate.—1 g. of $BaSO_4$ was boiled in a flask with a reflux tube for 15 minutes with 50 cc. of 3 n. Na_2CO_3 in which 10 g. of solid Na_2CO_3 were dissolved; the mixture was filtered; 10 cc. of 3 n. $HClO_4$ were repeatedly poured through the filter; and the residue was rinsed into a flask and compared with standards: it contained 5–10 mg. of Ba.

As to the action of sodium carbonate solution on anhydrous chromic sulfate see Noyes and Bray, *J. Am. Chem. Soc.*, 29, 158 (1907); also the following experiment.

75 mg. of Cr as anhydrous $Cr_2(SO_4)_3$ (the washed residue from the following experiment) was boiled for 20 minutes in a flask with a return condenser with 50 cc. of 5 n. Na_2CO_3. The residue was collected on a hardened filter and washed, and a hot 10-cc. portion of 3 n. $HClO_4$ was poured repeatedly through the filter: the solution was pale-green, and contained several milligrams of an extremely fine precipitate (which was removed by decantation, after several filtrations had failed). The Na_2CO_3 and $HClO_4$ solutions were found on analysis to contain 2 mg. and 4 mg. of Cr, respectively.

P. 8, N. 2.—Action of Hydrobromic, Perchloric, and Hydrofluoric Acids on Anhydrous Chromic Sulfate.—100 mg. of Cr as anhydrous $Cr_2(SO_4)_3$ (a lavender-grey material prepared by fuming $Cr(NO_3)_3$ with H_2SO_4 for several hours, washing the residue with water, and drying) were boiled for 20 minutes with 10 cc. of 9 n. HBr in a flask with a return condenser: the solution was distinctly green within 5 minutes, and the color continued to deepen during the boiling. The mixture was transferred to a casserole, and evaporated to 3 cc.: from the deep-green color of the solution and the size of the residue it was estimated that the solution contained 20–30 mg. of Cr. The mixture was then treated successively with HNO_3, $HClO_4$, and $HCHO_2$ as described in P. 5 and 6; and the chromium in the solution was determined by precipitating it with NH_4OH, igniting, washing with HF, and weighing as Cr_2O_3: the final solution contained 23.5 mg. of Cr.—For evidence that fuming $HClO_4$ does not dissolve anhydrous $Cr_2(SO_4)_3$ see the C. E. on page 303. It was concluded that 9 n. HBr dissolves anhydrous $Cr_2(SO_4)_3$ much more rapidly than either 16 n. HNO_3 or 9 n. $HClO_4$.—As to the solvent action of HCl on this material see C. E., P. 10, N. 2.

Another portion of anhydrous $Cr_2(SO_4)_3$ containing 100 mg. of Cr was digested on a steam-bath for 4 hours with 10 cc. of 27 n. HF, evaporated to 0.5 cc., and extracted with 10 cc. of water: the solution contained less than 0.2 mg. of Cr.

P. 9, N. 1.—Transformation of Silver Bromide into Chloride by Hydrochloric and Nitric Acids.—10 mg. of Ag as AgBr, left as a yellow residue after fuming a larger amount with $HClO_4$, were heated with a mixture of 5 cc. of 12 n. HCl and 1 cc. of 16 n. HNO_3: there was evident reaction at the surface of the AgBr, and nearly all the solid dissolved. The mixture was evaporated to a small volume, and diluted with water: a pure white precipitate formed (showing that little if any AgBr was present).

P. 9, N. 1.—Action of Nitric and Hydrochloric Acids on Metallic Rhodium and Iridium.—30 mg. of Rh, precipitated as metal by boiling

with $HCHO_2$, were treated twice with 10 cc. of 12 n. HCl and 1–2 cc. of 16 n. HNO_3, the mixture being evaporated nearly to dryness each time; then 5 cc. of 6 n. HCl were added, and the mixture was boiled and filtered: there was a large unattacked residue, and the solution was reddish. The solution was heated for a long time with H_2S at 90–100°: it gave a precipitate estimated to contain 3 mg. of Rh (showing that only this quantity of metal had dissolved in the acids).

20 mg. of Ir, precipitated as metal from $HClO_4$ solution by boiling with $HCHO_2$, were added to 5 cc. of 12 n. HCl and 0.5 cc. of 16 n. HNO_3, the mixture was evaporated slowly almost to dryness, 5 cc. of 6 n. HCl were added, and the brown solution was filtered: there was no residue (showing that the iridium had dissolved completely).

A mixture of 50 mg. of Pt and about 4 mg. of Ir and 4 mg. of Rh precipitated as metals from $HClO_4$ solution by boiling with 12 n. HCO_2H was heated with 1 volume of 16 n. HNO_3 and 4 volumes of 12 n. HCl, the mixture evaporated, the residue heated strongly with 9 n. $HClO_4$, and the mixture diluted: about one half of the total iridium and rhodium remained undissolved.

Wada and Nakazono, *Sci. Papers Inst. Phys. Chem. Research,* 1, 145 (1923), heated 100 mg. of Rh, precipitated by $Ti_2(SO_4)_3$, on a steam-bath for 10 minutes with 12 cc. of 6 n. HCl and 4 cc. of 6 n. HNO_3: 0.7 mg. of Rh passed into solution.—The experiment was repeated with 10 mg. of Rh: less than 0.2 mg. dissolved.—The experiment was repeated with a precipitated mixture of 50 mg. of Pt and 1 mg. of Rh: only 0.1 mg. of Rh remained undissolved.

P. 9, N. 2.—Removal of Chloride by Evaporation with Nitric Acid. —2 cc. of 12 n. HCl and 6 cc. of 16 n. HNO_3 were evaporated on a steam-bath to 2 cc.; to one half of this 9 cc. of water and 1 n. $AgNO_3$ were added: there was no turbidity.

To 500 mg. of Cl as $CaCl_2$ in 5 cc. of water 2 cc. of 16 n. HNO_3 were added, and the solution was boiled down over a flame to 2 cc., and in a second experiment to 0.5 cc.; the liquid was added to 5 cc. of 1 n. $AgNO_3$: a precipitate of AgCl resulted corresponding to 25 mg. of Cl in the first case, and to 20 mg. in the second.

P. 9, N. 3.—Volatilization of Mercuric Chloride on Evaporation with Nitric and Hydrochloric Acids.—To the number of milligrams of Hg as $HgCl_2$ shown in the first column of the following table were added the quantities of acid shown in the second column. These solutions were evaporated to dryness in a casserole on a steam-bath, and allowed to remain there 3–5 minutes. The residues were then dissolved; and the precipitates obtained with H_2S were compared with those given by known amounts of mercury. The results are given in the third column.

Milligrams taken	*Acid added*	*Milligrams in residue*	*Remarks*
2	1.0 cc. 12 n. HCl 2.0 cc. 16 n. HNO_3	0.5	——
2	0.5 cc. 6 n. HNO_3	2.0	——
2	0.5 cc. 6 n. HCl	2.0	——
2	12 cc 0.5 n. HCl	2.0	——
2	12 cc. 2.7 n. HNO_3	0.2	——
2	2 cc. 16 n. HNO_3	0.5	HNO_3 evaporated to dryness.
2	2 cc. 16 n. HNO_3	2.0	HNO_3 evaporated only to 0.5 cc.
2	11 cc. 3 n. HNO_3 1 cc. 6 n. HCl	1.0	Hg tested with NH_4Cl, NaOH, and KI.
1	11 cc. 3 n. HNO_3 1 cc. 6 n. HCl	0.3	Hg tested with NH_4Cl, NaOH, and KI.

2 mg. of Hg as $Hg(NO_3)_2$, instead of as $HgCl_2$, in 2 cc. of 16 n. HNO_3 were treated as in the preceding experiments: the residue contained the whole 2 mg.

To 2 cc. of solution containing 100 mg. of Hg as $HgCl_2$ were added the amounts of water and acid shown below in the first column. This mixture was distilled in a 50-cc. flask down to the volume shown in the second column; and the distillate was tested for mercury with NaOH, KI, and NH_4Cl. The milligrams found are shown in the last column.

Acid and water added	*Residual solution*	*Mercury in distillate*
0.3 cc. 6 n. HCl..... 2 cc. 16 n. HNO_3.....	0.2 cc.	4.0
0.3 cc. 6 n. HCl ..... 2 cc. 16 n. HNO_3..... 10 cc. of water.....	0.2	5.0
3 cc. 6 n. HCl.....	1.0	0.1
4 cc. 12 n. HCl.....	0.5	0.2
2 cc. saturated NaCl.....	1.5	0.0

A solution of 2 mg. of Hg as $HgCl_2$ in 0.5 cc. of 12 n. HCl was evaporated to 0.2 cc.; then 2 cc. of 16 n. HNO_3 were added; and the mixture was evaporated to 0.5 cc., diluted to 10 cc., and extracted with 10 cc. of ethyl acetate; from both layers the mercury was precipitated with H_2S: the aqueous layer contained 0.1 mg. of Hg, the ester layer about 2.0 mg.; showing that the $HgCl_2$ was neither volatilized nor converted into nitrate.

P. 9, N. 4.—Dissolving of Silver Chloride in Ammonium Hydroxide.—200 mg. of Ag as freshly prepared fused AgCl cut into small pieces were boiled with 5 cc. of 6 n. HNO_3 and 10 cc. of 12 n. HCl, the acid was evaporated, and the residue heated with 5 cc. of 15 n. NH_4OH and 10 cc. of 3 n. $NH_4C_2H_3O_2$ for 5 minutes: all except a few particles of the AgCl dissolved.

P. 10, N. 1.—Minerals Not Completely Decomposed by Acid Treatments.—See C. E., P. 3, N. 2.

P. 10, N. 2.—Decomposition of Materials by Fusion with Sodium Carbonate and with Potassium Bisulfate.—Each of the minerals named below left a large residue when 1 g. was treated with HNO_3 and HF as described in C. E., P. 3, N. 2. This residue was fused with Na_2CO_3 in the usual way: it remained largely unattacked. The large residue still remaining was fused with $K_2S_2O_7$ in a platinum crucible in the way described in P. 10, the melt extracted with water, and the residue digested with 6 n. HCl, and with HF (when necessary to remove SiO_2): in the cases of emery (Al_2O_3), rutile (TiO_2), zircon (ZrO_2-SiO_2), and monazite (Ce_2O_3, La_2O_3, ThO_2, P_2O_5) complete solution resulted; in the case of cassiterite (SnO_2) there was a residue of 450 mg.—In another experiment with monazite, the residue from the acid treatments was fused directly with $K_2S_2O_7$ (without first fusing with Na_2CO_3): complete solution resulted.

More than 500 mg. of Sn as ignited SnO_2 was treated with acids as in P. 2–7, and the residue was fused with Na_2CO_3: about 45 mg. of Sn went into solution. The residue, containing about 450 mg. of Sn, was fused with 5 g. of $K_2S_2O_7$ for 20 minutes, and then for 10 minutes longer, adding 2 g. more of $K_2S_2O_7$; the melt was boiled with 30 cc. of water, and the large residue filtered off; the filtrate was diluted and tested with H_2S: it contained only about 1 mg. of Sn. The residue was boiled with 10 cc. of 6 n. HCl, the mixture was filtered, and the filtrate tested for tin with H_2S (after dilution and partial neutralization of the acid): it contained about 40 mg. of Sn.

500 mg. of Ti as TiO_2 were fused with 5 g. of $K_2S_2O_7$ for 20 minutes, the melt was cooled, 4 cc. of 36 n. H_2SO_4 were added, the mixture was heated until fluid, and added to 50 cc. of water: everything dissolved and remained in solution upon boiling.

1 g. of chromite ($FeOCr_2O_3$) was fused in a "vitreosil" crucible with 10 g. of $K_2S_2O_7$ at a dull-red heat for 20 minutes; the crucible, after it had ceased to glow, was cooled suddenly by plunging its lower half into water and keeping it there till the melt was cold: the melt was easily removed. It was heated with 25 cc. of water for 2 hours, and the mixture was filtered: the filtrate was dark-green and the

residue light-green. The residue was heated on a steam-bath half an hour with 20 cc. of 6 n. HCl, and then 15 minutes longer with a fresh 20-cc. portion of 6 n. HCl: there was a small gritty residue (about 50 mg.) of black and white particles; the water extract contained roughly two thirds of the chromium, and the solutions from the first and second HCl treatments two thirds and one third of the remainder.

100 mg. of Cr as anhydrous $Cr_2(SO_4)_3$ (see C. E., P. 8, N. 2) were fused in a "vitreosil" crucible with 10 g. of $K_2S_2O_7$ at a dull-red heat for 20 minutes, the crucible was allowed to cool slowly, the melt (which was easily removed) was ground and treated with 25 cc. of water, the mixture was filtered, and the solution analyzed for chromium: it contained less than 1 mg. of Cr. (This result is different from that in the preceding experiment with chromite.) The green residue was heated for 1 hour with 10 cc. of 12 n. HCl in a covered casserole on a steam-bath, the mixture was then evaporated to 1 cc., diluted, and filtered: the filtrate contained 36 mg. of Cr. The residue was then digested with 10 cc. of 12 n. HCl on a steam-bath for 5 hours: the solution contained 25 mg. of Cr. Finally the residue was boiled with 25 cc. of 12 n. HCl in a flask with a return condenser: it dissolved completely in about 12 hours.—To determine the action of HCl on the original material, another portion of the anhydrous $Cr_2(SO_4)_3$ containing 100 mg. of Cr was digested for 6 hours with 10 cc. of 12 n. HCl in a covered casserole on a steam-bath; the mixture was evaporated to 1 cc., diluted, and filtered: the filtrate contained 12 mg. of Cr (showing that the original material dissolves in HCl much less rapidly than the residue after the fusion).

Behavior of Metallic Rhodium on Fusion with Potassium Bisulfate.—Wada and Nakazono, *Sci. Papers Inst. Phys. Chem. Research,* 1, 144 (1923), fused 100 mg. of Rh, precipitated by $Ti_2(SO_4)_3$, with 10 g. of $K_2S_2O_7$ for 5–10 minutes, and treated the melt with water: all the Rh dissolved.

P. 10, N. 6.—Acidity of Potassium Bisulfate after Fusion.—Known fractions of the solution obtained by fusing 10 g. of $K_2S_2O_7$ as in P. 10 and dissolving the melt in water were titrated with standard NaOH solution: 55 milliequivalents of acid were found to be left after the fusion, while similar analyses of a sample of $K_2S_2O_7$ showed that the 10 g. originally contained about 79 milliequivalents of acid.

P. 10, N. 8.—Action of Fused Potassium Bisulfate on Platinum.—10 g. of $K_2S_2O_7$ were fused in a platinum crucible for 20 minutes as described in P. 10. To the aqueous solution were added 2 drops of 6 n. HCl and 1 cc. of precipitated Ag, and the mixture was shaken: there was a distinct blackening of the silver, which by comparative tests was

estimated to correspond to at least 0.5 mg. of Pt.—The experiment was repeated, except that the temperature of fusion was higher and that the resulting melt was heated in the crucible with concentrated H_2SO_4 for 25 minutes: the amount of platinum was estimated to be about 2 mg.

P. 11, N. 1, 2.—Behavior of Substances on Fusion with Sodium Peroxide and Treatment of the Melt with Water.—As to the fusion of various substances with Na_2O_2 see Leidié and Quennessen, *Bull. soc. chim.*, (3), 27, 179–183 (1902); Dudley, *Am. Chem. J.*, 28, 59–66 (1902).

The quantities of the various substances shown in the following table were added to 5 g. of Na_2O_2 fused in a nickel crucible, and the

Substance treated		*Minutes fused*	*Aqueous extract*		*Result on heating with HCl*
Nature	*Mg.*		*Mg.*	*Color*	
Pt, metal	500	75	0 Pt	Very pale yellow	[a]Dense yellow residue; deep-yellow solution.
Ir, metal	500	75	0.5 Ir	" " "	[a]Complete solution, dark blue turning dark red.
Ir, metal	500	20	—	" " "	Complete solution.
Rh, metal	100	20	Small	—	[a]Almost complete solution, dark orange-yellow.
Pd, metal	50	5	2–3 Pd	Pale yellow	[a]Complete solution, brown.
Os, metal	200	20	Large	Dark orange	See C. E., N. 4, below.
Ru, metal	500	20	Large	Dark orange-red	See C. E., N. 4, below.
Alloy of 32% Os, 50% Ir, 10% Ru, 4% Pt	1000	15	—	Dark colored	Complete solution, deep color.
"Osmium-iridium"	500	20	—	——	Complete solution.
Sn as ignited SnO_2	500	1	250	Colorless	[a]Complete solution.
SiC (carborundum)	500	5–20	—	——	All dissolved except small gelatinous residue.
Ferrosilicon, 89% Fe, 13% Si	500	"	—	——	Complete solution.
Ferrochrome, $FeCr_x$	500	"	—	——	Complete solution.
MoS_2 (molybdenite)	500	"	—	——	Complete solution.
Platinum ore (Pt, Pd, Os, Ir)	500	"	—	——	Complete solution.

fusion was continued for the time shown in the third column. The melt was then treated with 75–100 cc. of water. In five of the experiments, designated by *a* in the last column, the alkaline solution was filtered or decanted off; and the residue was heated with 12 n. HCl. In the other experiments, 12 n. HCl was added to acid reaction, and then 3–5 cc. more; and the mixture was boiled for 5–10 minutes, unless a clear solution previously resulted. The results are shown in the last three columns.

As to the effect of fusing Al_2O_3, SnO_2, and TiO_2 with KOH see Noyes and Bray, *J. Am. Chem. Soc.*, **29**, 159 (1907).

P. 11, N. 3.—Action of Fused Sodium Peroxide on Nickel and Silver Crucibles.—5 g. of Na_2O_2 were fused at a low-red heat for 20 minutes in a 35-cc. nickel crucible weighing 17 g. The crucible was washed out and dried: it was found to have lost 1 g. in weight.

5 g. of Na_2O_2 were melted in a 35-cc. nickel crucible, 500 mg. of Sn as SnO_2 were added, and the fusion continued one minute; the melt was extracted with water and the residue dissolved in HCl, and tested for nickel: it was estimated to contain 450 mg.

For the composition of the hydrated oxide of nickel produced see Dudley, *J. Am. Chem. Soc.*, **18**, 901 (1896).

2 g. of Na_2O_2 were fused on a silver crucible cover for 20 minutes: the cover lost in weight 0.9 g.

P. 11, N. 4.—Decomposition of Sodium Peroxide Solution by Heating.—5 g. of Na_2O_2 were dissolved in 30 cc. of water, and the mixture heated on a steam-bath for 10 minutes; the solution was then tested for H_2O_2 by acidifying and adding titanium solution: no color resulted.

Volatilization of Osmium and Ruthenium Tetroxides from Boiling Solutions of Sodium Peroxide and of Hydrochloric Acid.—10 mg. of Os and 10 mg. of Ru in separate experiments were added to 30 cc. of water in which 5 g. of Na_2O_2 had been dissolved, and the mixture was boiled 4 minutes in a distilling flask till 3–4 cc. of distillate had passed over into a NaOH solution: in both experiments the distillate was colorless, and in the ruthenium experiment it gave no precipitate with C_2H_5OH (showing that there was no volatilization of either element).

200 mg. of Os were fused with 5 g. of Na_2O_2, the melt was treated with water, the mixture was acidified with 12 n. HCl, and distilled for 5 minutes into 6 n. NaOH: a dark-orange distillate resulted. The mixture was distilled 3 minutes longer into fresh 6 n. NaOH: the distillate was yellow and contained 4–5 mg. of Os. 25 cc. of 16 n. HNO_3 were added to the residual solution, and the mixture distilled 10 minutes into fresh 6 n. NaOH: a pale yellow distillate giving no test for osmium resulted.

The experiment was repeated using 500 mg. of Ru (in place of 200 mg. of Os), except that no HNO_3 was added at the end: the first distillate was pale-yellow (probably from the presence of 1–2 mg. of Os as impurity); the second distillate was colorless.

P. 11, N. 5.—Action of Concentrated Hydrochloric and Nitric Acids on Platinum Oxide.—500 mg. of Pt were fused with 5 g. of Na_2O_2 for 75 minutes, and the melt was treated with water: there was a coal-black residue. The residue was filtered out and boiled for a long time with 12 n. HCl, then with HCl and HNO_3: a large dense yellow residue remained, but the solution also contained much platinum.

P. 11, N. 6.—Transformation of the Yellow Oxide of Platinum into Sulfide.—The dense yellow residue of Pt_2O_3, undissolved in the preceding experiment, was allowed to stand in the cold over night under water saturated with H_2S: it was completely converted to a black sulfide, and this dissolved readily in a mixture of HCl and HNO_3.

Precipitation of Tungstic Acid by Hydrochloric Acid.—3 mg. of W as Na_2WO_4 were added to 50 cc. of 0.6 n. HCl containing 5 g. of NaCl, the solution was saturated with H_2S, and heated in a boiling water-bath for one hour: there was a precipitate (of H_2WO_4) corresponding to 1 mg. of W. The mixture stood in the cold three hours: 2.5 mg. of W had separated.

P. 11, N. 7.—Dissolving of Sulfides of the Platinum Elements in Hydrobromic Acid, Bromine, and Nitric Acid.—10 mg. of Os and 10 mg. of Ru as sulfides were separately heated with 10 cc. of 9 n. HBr and 2 cc. of liquid Br_2 in a covered casserole on a steam-bath for 2 hours: nearly all the osmium, but very little of the ruthenium, dissolved. 3 cc. of 6 n. HNO_3 were added: the remaining sulfides dissolved instantly, except that in the case of ruthenium there was a very small fine metallic residue.

20 mg. of Ir as sulfide were heated with 10 cc. of 9 n. HBr and a few drops of liquid Br_2 in a flask on a steam-bath for 10 minutes: the sulfide dissolved completely.

100 mg. of Pt as PtS_2 were heated with 10 cc. of 9 n. HBr and 2 cc. of Br_2 in a covered casserole on a steam-bath for one hour: the Br_2 was not used up, and very little PtS_2 dissolved. 8 cc. of 6 n. HNO_3 were now added: the precipitate dissolved immediately, except for a small metallic-appearing residue of 5–10 mg., which quickly dissolved in HCl and HNO_3.

ANALYSIS OF THE SELENIUM GROUP

P. 21, N. 1, 2.—Precipitation of Selenium by Hydroxylamine.—To 50 mg. of Se as H_2SeO_3 in 5 cc. of water and 7 cc. of 9 n. HBr were added 5 drops of liquid Br_2, and the solution was then decolorized by adding 3 f. NH_2OHHCl drop by drop: a small reddish precipitate formed. 1 cc. more 3 f. NH_2OHHCl was added, and the mixture heated for five minutes in a test-tube partly immersed in boiling water: a large red precipitate formed, which darkened on standing. The mixture was cooled and filtered, and the filtrate saturated with H_2S: no precipitate formed even on standing 15 minutes, showing that the precipitation of the selenium had been complete and that no sulfur is liberated from H_2S by NH_2OH or its oxidation-products.

To 50 mg. of Se as H_2SeO_3 in 5 cc. of water and 7 cc. of 9 n. HBr was added 1 cc. of 3 f. NH_2OH, and the solution was allowed to stand 1–2 minutes: no precipitate formed. The solution was heated to 40–50°: a finely divided red precipitate began to separate. The mixture was then heated for 5 minutes on a steam-bath in a covered conical flask: the precipitate coagulated and darkened. The precipitate was filtered out, and the solution again heated and allowed to stand 4–5 minutes: no more precipitate formed. The solution was then saturated with SO_2 gas, and 1 cc. of 1 n. KI added: no precipitate formed, thus showing that, although the precipitation of Se in a strongly acid solution by NH_2OH is slow in the cold, it is made complete in 5 minutes by heating.

To 0.5 mg. of Se in 7 cc. of 9 n. HBr and 5 cc. of water was added 1 cc. of 3 f. NH_2OH, and the mixture was heated in a test-tube to 60–80° for 2½ minutes: a fine red precipitate separated throughout the solution, showing that the test will detect 0.5 mg. or less.

Precipitation of Selenium by Hydrazine.—To 50 mg. of Se as H_2SeO_3 in 5 cc. of water and 7 cc. of 9 n. HBr were added 5 drops of liquid Br_2, and the solution was then decolorized with 0.1 f. $N_2H_6SO_4$ added a few drops at a time: a small reddish precipitate formed. 6 cc. of 0.1 f. $N_2H_6SO_4$ were added, and the mixture allowed to stand in the cold for 5 minutes: a fine red precipitate separated which filtered with difficulty. The filtrate was heated to 60–80°: more red precipitate formed. This mixture was then heated for 5 minutes on a steam-bath, filtered, and the filtrate saturated with H_2S: only an insignificant turbidity resulted, showing that, although the precipitation of Se by N_2H_4 is slow in a cold acid solution, it is made complete in 5 minutes by heating.

P. 21, N. 3.—Non-Volatility of Germanium in the Selenium Precipitation.—2 mg. of Ge as Na_2GeO_3 were added to 7 cc. of 9 n. HBr and

5 cc. of water containing 50 mg. of Se. 1 cc. of 3 f. NH_2OHHCl was added, and the solution heated on a steam-bath in a covered conical flask for 5 minutes. The mixture was cooled, the dark-red precipitate filtered out, the filtrate saturated with H_2S, and the precipitate of GeS_2 formed compared with that from a standard solution: no loss of germanium could be observed.

P. 21, N. 3.—Non-Reduction of Quinquivalent Arsenic by Hydroxylamine in Hydrobromic Acid Solution.—To a solution containing 10 mg. of As as As_2O_5 in 7 cc. of 9 n. HBr and 5 cc. of water were added 2 drops of saturated Br_2 solution; the solution was decolorized with 1 f. $NH_2OHHClO_4$ and 3 cc. more were added. It was then heated for 5 minutes in a test-tube immersed in boiling water, and cooled to room temperature. To one half of it was added 1 cc. of 1 n. KI: iodine was formed at once, and its amount showed that little if any H_3AsO_4 had been reduced by NH_2OH.—In the experiment described in the following section, the slow precipitation of arsenic by H_2S at room temperature shows that much quinquivalent arsenic had remained after the previous treatment with NH_2OH.

P. 22, N. 1.—Precipitation of Quinquivalent Arsenic by Hydrogen Sulfide from 5-Normal Hydrobromic Acid.—As to the action of H_2S on H_3AsO_4 at various concentrations of added acid, the formation of H_3AsO_3S, and its decomposition to yield S and a compound of trivalent arsenic, see McCay, *Z. anorg. Chem.*, 29, 36 (1902); Usher and Travers, *J. Chem. Soc. London*, 87, 1370 (1905).

A solution of 100 mg. of As as As_2O_5 in 7 cc. of 9 n. HBr, 5 cc. of water, and 2 cc. of 3 f. $NH_2(OH)HCl$ was heated for five minutes, then cooled, a moderately rapid current of H_2S passed in for 2 minutes, and the solution filtered: a yellow precipitate was collected and a white finely divided precipitate of sulfur ran through the filter. The filtrate was heated: more precipitate formed and coagulated. This was filtered out, and H_2S was again passed into the filtrate for 2 minutes: more yellow precipitate formed. This was filtered out, the filtrate saturated with H_2S, and allowed to stand 30 minutes: no more precipitate separated, showing that the quinquivalent arsenic had been completely precipitated by the preceding treatments.

P. 22, N. 2, 3.—Precipitation of Germanium by Hydrogen Sulfide from Acid Solutions.—See Gmelin-Kraut, *Handbuch der anorganischen Chemie*, IV, 1, 226 (1911), for a summary of the results of Winkler, *J. prakt. Chem.* [2], 34, 177; 36, 177 (1887). Dennis and Papish, *J. Am. Chem. Soc.*, 43, 2139 (1921), have found that, in washing GeS_2 with H_2SO_4 solution saturated with H_2S, 3 n. acid is less satisfactory than 5 n.

25 mg. of Ge as Na_2GeO_3 were dissolved in 7 cc. of 9 n. HBr, 5 cc. of water, and 2 cc. of 3 f. NH_2OHHCl, and a fairly rapid current of H_2S passed through the solution for 2 minutes: a large flocculent white precipitate separated and coagulated. The mixture was heated to 70–80° for 2–3 minutes, cooled, H_2S again passed in for 2 minutes, the precipitate filtered out, the filtrate saturated with H_2S, and allowed to stand for 30 minutes: no more precipitate formed, showing that the germanium had been completely precipitated.

H_2S was passed for 2 minutes through a solution containing 1 mg. of Ge in 7 cc. of 9 n. HBr, 5 cc. of water, and 1 cc. of 3 f. NH_2OHHCl: a white coagulated precipitate formed within the 2 minutes.

P. 22, N. 3.—Delicacy of the Precipitation of Arsenic Sulfide and its Color Detection in the Presence of Germanium.—Through a solution containing 1 mg. of As as As_2O_5 and 25 mg. of Ge in 7 cc. of 9 n. HBr and 5 cc. of water H_2S was passed for 2 minutes, the solution was then heated to 70–80°, cooled, and again treated with H_2S for 2 minutes: the precipitate was white in the cold, but became distinctly yellowish after the mixture was heated and treated with H_2S the second time, showing that even 1 mg. of arsenic will precipitate and be apparent even in the presence of a large amount of germanium.

P. 22, N. 4.—Reduction of Quinquivalent Antimony by Hydroxylamine.—To a solution containing 10 mg. of Sb as $SbCl_3$ in 7 cc. of 9 n. HBr and 5 cc. of water was added 1 cc. of saturated Br_2 solution; the solution was then decolorized with 3 f. NH_2OHHCl, and 1 cc. more added. The solution was divided into two equal portions. One portion was heated on a steam-bath for 5 minutes and then cooled; and to it was added 1 cc. of 1 n. KI: no I_2 was liberated, showing that the NH_2OH had completely reduced the antimony in the hot solution. To the other portion was added 1 cc. of 1 n. KI: no iodine was liberated, showing that even in the cold the antimony had been reduced by the NH_2OH.—This experiment was repeated using only 5.5 cc. of 9 n. HBr: with this smaller concentration of HBr the antimony was not completely reduced at room temperature, but the reduction was complete in the hot solution.

P. 22, N. 4.—Non-Precipitation of Antimony by Hydrogen Sulfide from Hydrobromic Acid and from Hydrofluoric Acid Solutions.—To 10 mg. of Sb as $SbCl_3$ in 7 cc. of 9 n. HBr and 5 cc. of water were added 50 mg. of Br_2, enough Na_2SO_3 to almost decolorize the solution, and 1 cc. of 3 f. NH_2OHHCl; and then (without heating) the solution was saturated with H_2S: no precipitate formed.

To 2 mg. of Sb as $SbCl_3$ in a platinum dish were added 6 cc. of 6 n. NH_4OH and 4 cc. of 27 n. HF; and the cold solution was saturated

with H_2S: no precipitate formed. To this solution were added 3 drops of a solution of $SbCl_3$ containing 10 mg. of Sb, and the solution was again saturated with H_2S: no precipitate formed.

Solubility of Antimony Trisulfide in Ammonium Hydroxide.—10 mg. of Sb as $SbCl_3$ were precipitated by H_2S, the precipitate was washed, and a 6-cc. portion of 6 n. NH_4OH was poured repeatedly through the filter; the solution was then acidified and saturated with H_2S: a precipitate containing about 0.2–0.3 mg. of Sb formed.

Behavior of Tellurium with Hydroxylamine and with Hydrogen Sulfide in Hydrobromic Acid Solution, and of its Decomposed Sulfide Precipitate with Ammonium Hydroxide.—A solution of 10 mg. of Te as TeO_2 in 7 cc. of 9 n. HBr and a drop of Br_2 was treated by P. 21, 22, and 23: a trace of selenium (present as impurity), but no tellurium, was precipitated by NH_2OH when the solution was heated. H_2S was passed in at room temperature: a flocculent precipitate separated, which was brownish-black, but became much more compact and pure black in color when the mixture was heated in a stoppered bottle. (The filtrate from the H_2S precipitate was diluted to 100 cc., saturated with H_2S and allowed to stand: there was no precipitate.) The precipitate on the filter was extracted repeatedly with a 6-cc. portion of 6 n. NH_4OH: no tellurium dissolved, showing it to be present as metal; for undecomposed TeS_2 dissolves in NH_4OH (see the last paragraph on this page).

The experiment was repeated, except that 50 mg. of As as As_2O_5 were also present: the H_2S precipitate was orange in color, and on heating showed little change in density or color. It was extracted with a 10-cc. portion of 6 n. NH_4OH: a large, finely divided black residue remained on the filter (showing that little if any tellurium dissolves even when much arsenic is present).

The first part of the first experiment was repeated except that 14 cc. of water were added: as before, only the selenium impurity was precipitated by NH_2OH. The filtrate was heated on a steam-bath in a covered flask for 30 minutes: there was no precipitate (showing that tellurium is not precipitated by NH_2OH from 3 n. HBr).

Decomposition of Tellurium Sulfide into Tellurium and Sulfur.—A solution of 10 mg. of Te as TeO_2 in 1 cc. of 6 n. HCl was diluted to 20 cc., and treated with H_2S for about 30 seconds at room temperature; the brownish precipitate was immediately filtered, washed, and repeatedly extracted on the filter with a 10-cc. portion of 6 n. NH_4OH: at least two thirds of the precipitate dissolved in 12 treatments. It was concluded that the tellurium is precipitated at room temperature as TeS_2, and that when heated this changes to elementary tellurium.

Becker, *Ann. Chem.*, **180**, 260 (1875), showed that from a precipitate formed by the action of H_2S on a solution of H_2TeO_3 over 90% of the sulfur can in several hours be extracted by CS_2; and he concluded that TeS_2, if formed, decomposes readily into Te and S.

P. 23, N. 1.—Precipitation of Quinquivalent Arsenic by Hydrogen Sulfide from Hydrofluoric Acid Solution.—200 mg. of As as As_2O_5 in 5 n. HCl were precipitated with H_2S, the precipitate was washed and dissolved in 12 cc. of 6 n. NH_4OH, the solution transferred to a platinum dish, 8 cc. of 27 n. HF added, and H_2S passed in for 5 minutes; the precipitate was filtered out, the filtrate heated to 70–80° for 3–4 minutes, cooled, and again saturated with H_2S: no precipitate formed. 10 cc. of 12 n. HCl were then added, and the solution was again saturated with H_2S: again no precipitate formed, showing that all the arsenic had been precipitated fairly rapidly from the 7 n. HF.

1 mg. of As as As_2O_5 was precipitated with H_2S from a 4–5 n. HBr solution, the precipitate dissolved in 6 cc. of 6 n. NH_4OH, the solution transferred to a platinum dish, 4 cc. of 27 n. HF added, and the solution saturated with H_2S: a yellow precipitate corresponding to 1 mg. of As separated.

As to the slow precipitation of quinquivalent arsenic by H_2S from 3 n. HF, see C. E., D. 39.

P. 23, N. 1.—Non-Precipitation of Germanium by Hydrogen Sulfide from Hydrofluoric Acid Solution and its Separation from Arsenic.—25 mg. of Ge as solid Na_2GeO_3 were dissolved in 6 cc. of 6 n. NH_4OH, the solution transferred to a platinum dish, 5.5 cc. of 27 n. HF added, and the solution saturated with H_2S: no precipitate formed. The solution was then diluted, first with 5 cc. and then with 15 cc. of water, and saturated with H_2S after each dilution: in neither case did a precipitate form.

As to the separation of trivalent arsenic from germanium by H_2S in 4–9 n. HF, see Müller, *J. Am. Chem. Soc.*, **43**, 2549 (1921).

500 mg. of As as $AsCl_3$ and 1.5 mg. of Ge as Na_2GeO_3 were precipitated from a 6 n. HCl solution by H_2S; the precipitate was filtered with the aid of suction, sucked dry, and dissolved on the filter with 20 cc. of 6 n. NH_4OH; the solution was transferred to a platinum dish, 17–18 cc. of 27 n. HF added: a large precipitate of As_2S_3 formed at once. The mixture was saturated with H_2S; the precipitate was filtered out, 5 cc. of 6 n. H_2SO_4 added, the solution evaporated until the H_2SO_4 fumed, cooled, diluted to 30 cc. and saturated with H_2S: a white precipitate formed, and was estimated by comparison with a standard to contain 0.8–1.2 mg. of Ge, showing that all the arsenic had been precipitated from the HF solution and that only a small amount of germanium had been carried out with it.

In another experiment 25 mg. of Ge and 1 mg. of As as As_2O_5 were precipitated from a 4–5 n. HBr solution, the precipitate dissolved in 6 cc. of 6 n. NH_4OH, the solution transferred to a platinum dish, and 4 cc. of 2 n. HF added; the mixture was saturated with H_2S: a small yellow precipitate, corresponding to 1 mg. of As, separated.

P. 25, N. 1, 2.—Precipitation of Germanium by Hydrogen Sulfide from 5-Normal Sulfuric Acid.—See Winkler, *J. prakt. Chem.* (2), **34**, 177 (1886); Dennis and Papish, *J. Am. Chem. Soc.*, **43**, 2135 (1921).

1 mg. of Ge as GeO_2 in HF was treated by the first paragraph of P. 25: the solution became distinctly turbid in 3 minutes, and the precipitate settled out on standing over night. When collected on a filter it had a faint yellow shade, indicating the presence of some sulfur.—In several control experiments without the germanium, a faint turbidity due to sulfur appeared within 30 to 60 minutes; it slowly increased, but remained in suspension on standing over night.

P. 25, N. 4.—Precipitation of Potassium Fluogermanate Alone and in the Presence of Arsenic.—See Wada and Kato, *Sci. Papers Inst. Phys. Chem. Research*, **3**, 254 (1925).

The H_2S precipitate obtained with 1 mg. of Ge in the experiment described above was treated by the second paragraph of P. 25: the solution became turbid when the K_2CO_3 was added; and, after the heating, the coagulated precipitate was easily seen.

A solution of 1.5 mg. of Ge as Na_2GeO_3 and 0.1 g. of KNO_3 in 16 n. HNO_3 was evaporated just to dryness, the residue was dissolved in 2 cc. of water and transferred to a platinum crucible, 2 cc. of 27 n. HF were added, and the solution was evaporated just to dryness; the residue was dissolved in 5 drops of 27 n. HF and 1 cc. of water, and the mixture was heated to boiling and allowed to stand for 15 minutes: the characteristic precipitate of K_2GeF_6 was seen when the crucible was slowly turned and tilted. The precipitate was collected on a filter, washed with a little cold saturated K_2SO_4 solution, and dissolved in 5 cc. of hot 6 n. H_2SO_4; the solution was evaporated to fuming in a platinum dish, 10 cc. of 3.5 n. HCl were added, the cold solution in a test-tube was saturated with H_2S, the tube was cooled, and allowed to stand: a white precipitate of GeS_2 appeared within 5 minutes and settled out on standing.

The last experiment was repeated with a mixture of 1.5 mg. of Ge, 500 mg. of As, and 0.1 g. of KNO_3: a satisfactory K_2GeF_6 precipitate resulted, and this yielded after careful washing a small white precipitate in the subsequent test with H_2S.

The experiment was repeated with a mixture of 1 mg. of Ge as Na_2GeO_3, 1 mg. of As as As_2O_5, and 0.1 g. of KNO_3: the test for germanium and the confirmation with H_2S were satisfactory.

ANALYSIS OF TUNGSTEN AND TANTALUM GROUPS

GENERAL DISCUSSION

D. 30.—Precipitation of Tungstic Acid by Evaporation with Sulfuric Acid and Dilution.—To 2 mg. of W and 4 mg. of W as Na_2WO_4 2 cc. of 36 n. H_2SO_4 were added, and the solutions evaporated to the fuming point: even after cooling the solutions remained clear. The liquid was added to 5 cc. of water: a white turbidity appeared in 3–5 minutes in the 4-mg. portion, and in 30 minutes in the 2-mg. portion; on standing over night, yellow precipitates had settled out in both cases.—The experiment, with some variations, was many times repeated with 1 mg. of W: in no case did any precipitate separate, even on standing.

To 2 mg. of W as Na_2WO_4 were added 2 cc. of 27 n. HF, 0.5 cc. of 16 n. HNO_3, and 3 cc. of 36 n. H_2SO_4; the solution was heated gently until most of the HF was expelled; it was then heated at 110° in a hot closet for 30 minutes; and finally it was added to 8 cc. of water: a precipitate separated almost immediately.—The experiment was repeated, except that the mixture was heated on a sand-bath just below the fuming point for 30 minutes: upon dilution a precipitate began to separate.

Mixtures of 2 mg. of W and 100 mg. of Mo (in two experiments) and of 4 mg. of W and 100 mg. of Mo, as sulfides, were heated with 8 cc. of 16 n. HNO_3 and 2 cc. of 12 n. HCl on a steam-bath. To the clear solution were added 3 cc. of 36 n. H_2SO_4, the mixture was evaporated to slight fuming, kept at this temperature for 5 minutes, and cooled; 5 cc. of water were added: during the heating with H_2SO_4 a yellow precipitate separated from the mixture containing 4 mg. of W; in one of the mixtures containing 2 mg. of W there was an extremely small but distinct precipitate, but in the other there was no precipitate even on standing over night.

D. 39.—Precipitation of Elements from 3-Normal Hydrofluoric Acid by Hydrogen Sulfide.—Solutions 3 n. in HF containing the number of milligrams of the elements shown in the first column of the table on the next page were made from the substances shown in the second column; the total volumes are given in third column. H_2S was passed into the solution at room temperature for the times shown in the fourth column; the precipitates, described in the fifth column, were filtered off; and the filtrates were analyzed when necessary by the methods shown in the last column.

For other experiments on the precipitation of elements from fluoride solutions, see C. E. on P. 23, N. 1, and on P. 132, N. 1–2; also Wada and Kato, *Sci. Papers Inst. Phys. Chem. Res.*, **3**, 248 (1925).

Element	*Substance*	*Volume in cc.*	*Time, minutes*	*Precipitate*	*Filtrate*	*Method of analyzing filtrate*
1 Bi	$Bi(NO_3)_3$	45	15	Black	0 Bi	
100 Bi	"	"	"	Large	0 Bi	Evaporate with H_2SO_4, add NH_4OH.
1 Cu	$CuSO_4$	"	"	Black	0 Cu	
100 Te	TeO_2	27	"	Large	0 Te	Evaporate, add HCl, H_2S.
100 Se	SeO_2	27	"	"	0 Se	Evaporate, add HCl, H_2S.
2 As	H_3AsO_4	45	50	None	2 As[a]	
500 As	"	"	60	Large	Large As	Let stand, add more H_2S.
1 Sb[b,c]	Sb_2O_5	"	15	Orange	0 Sb	
500 Sb	"	"	30	Large	250 Sb	Evaporate with H_2SO_4, add water and H_2S.
500 Sn	$SnO(OH)_2$	"	60	None	500 Sn	
500 Sn 1 Sb	$SnO(OH)_2$ Sb_2O_5	"	10	Orange, small	500 Sn 0 Sb	
2 Sn[d] 500 Sb	$SnO(OH)_2$ Sb_2O_5	"	30	Large	1 Sn Large Sb	Evaporate with H_2SO_4, add Zn, then $HgCl_2$.
6 Pb	$Pb(NO_3)_2$	"	10	Small	5 Pb	
500 W	Na_2WO_4	27	60	None	500 W	
300 Mo	$(NH_4)_2MoO_4$	45	30	Large	56 Mo[e]	
100 Mo[f] 4 W	$(NH_4)_2MoO_4$ Na_2WO_4	"	"	"	Large Mo 3 W	Evaporate with H_2SO_4.

[a] The solution containing 2 mg. of As as H_3AsO_4 in 3 n. HF was heated on a steam-bath, and H_2S passed in: a precipitate appeared almost immediately.

[b] 1 mg. of Sb as Sb_2O_5 in 30 cc. of 4.5 n. HF gave no precipitate with H_2S in 30 minutes at room temperature, but a distinct precipitate separated when the solution was cooled by placing the platinum dish in ice water.

[c] 1 mg. of Sb as Sb_2O_5 in 45 cc. of 3 n. HF and 1 cc. of 36 n. H_2SO_4 gave no precipitate with H_2S.—This experiment was repeated with 2 mg. of Sb: a distinct, compact, orange precipitate separated.

[d] The experiment was repeated with a mixture of 500 mg. of Sb and 1 mg. of Sn: no precipitate of HgCl was obtained.

[e] The filtrate became turbid on short standing. It was heated on a steam-bath, and H_2S passed in for 30 minutes more; the precipitate was filtered off, converted into MoO_3 by HNO_3 and weighed: it contained 26 mg. of Mo. The filtrate from the second H_2S precipitate was evaporated with HNO_3, and the resulting MoO_3 weighed: it contained 30 mg. of Mo.

[f] A mixture of 400 mg. of Mo, 2 mg. of Ta, 2 mg. of Ti, 2 mg. of Sn, and 4 mg. of W in 45 cc. of 3 n. HF was treated with H_2S, first at room temperature and then at 90–100°: the solution became very dark-colored, but very little precipitate separated. Then 3 cc. of 36 n. H_2SO_4 were added: a very bulky, slimy precipitate instantly separated. The mixture was filtered: the liquid ran through the filter with extreme slowness. The filtrate was analyzed for all the elements present in small quantity: no test was obtained for any of them except tantalum.—A mixture of 400 mg. of Mo, 8 mg. of Sn, and 8 mg. of W in 45 cc. of 3 n. HF and 2 cc. of 36 n. H_2SO_4 was treated with H_2S for 30 minutes, the large precipitate was filtered off, and the filtrate analyzed: it contained about 6 mg. of Sn and 7 mg. of W.

D. 44.—Failure to Separate Columbium from Titanium by Addition of Acid after Precipitation by Ammonium Hydroxide.—1 mg. of Cb as $HCbO_3$ was dissolved in 10 cc. of 1 f. H_2O_2 and 2 cc. of 7 n. HCl, SO_2 gas was passed in to saturation (to reduce the H_2O_2), 6 n. NH_4OH was added to distinct alkaline reaction, the mixture was allowed to stand for 3 minutes, and then one fourth of its volume of 12 n. HCl was added: the NH_4OH precipitate remained in large part undissolved.

The experiment was repeated with 100 mg. of Ti as $TiO(OH)_2$: the NH_4OH precipitate dissolved completely.

The experiment was repeated with a mixture of 2 mg. of Cb and 50 mg. of Ti, and with one of 5 mg. of Cb and 100 mg. of Ti: the NH_4OH precipitate dissolved completely in the first case, and nearly so in the second case.

D. 46.—Partial Separation of Tantalum from Titanium and Columbium by Hydrogen Peroxide and Hydrochloric Acid.—Many experiments were made by the following process. The tantalum and tungsten groups were separated by a treatment similar to that in P. 30, except that 10 cc. of $(NH_4)_2S$ reagent were used and the mixture was heated at 50–60° in a covered casserole (instead of at 100° in a pressure bottle). The $(NH_4)_2S$ precipitate was digested with 3 n. NH_4OH only when it had an orange color (due to molybdenum). To the $(NH_4)_2S$ precipitate in a casserole were added 5–15 cc. of 1 f. H_2O_2 and 1–3 cc. of 7 n. HCl; the mixture was heated till the H_2O_2 began to decompose rapidly, stirred for 2 or 3 minutes, and filtered through a HF-washed filter. (If the residue was large and the solution strongly colored, showing the presence of much *titanium,* the residue was dissolved in HF, and the process was repeated.)—The residue was dissolved in HF and any *tantalum* in it precipitated as potassium oxyfluotantalate as in P. 47.—The H_2O_2 solution was evaporated to strong fuming with 1–2 cc. of 36 n. H_2SO_4, cooled, and poured into 5 cc. of 1 n. HCl. One third of this solution was poured through a Zn column into $HgCl_2$ solution (see P. 48). If there was a precipitate (showing the presence of *columbium,* tungsten, or molybdenum), the remaining two thirds of the solution was treated with NH_4OH in excess, filtered, and the filtrate rejected; the precipitate was heated in a platinum crucible till dry, the residue was mixed in a mortar with six times its volume of a mixture of equal weights of Na_2CO_3 and S, and heated in a covered porcelain crucible to a dull-red heat for 15 minutes, and cooled. The melt was treated with successive portions of hot water till it disintegrated, the residue was collected on a quantitative filter, and washed. The filtrate was united with the $(NH_4)_2S$ solution of the tungsten group (or tested for tungsten directly). The

residue from the fusion was dissolved in HF, evaporated to fuming with 1–2 cc. of 36 n. H_2SO_4, cooled, and poured into 5 cc. of 1 n. HCl; this solution was then poured through a Zn column into $HgCl_2$ solution: a precipitate now proved the presence of *columbium*.

1 and 20 mg. of Ta as Ta_2O_5 in HF were treated separately by the foregoing process, except that the H_2O_2 solution was tested for tantalum by saturating it with SO_2 and adding NH_4OH: in each experiment about half the tantalum was found in the H_2O_2 solution and the other half (not dissolved by H_2O_2 and HCl) was precipitated as the oxyfluotantalate.

100 mg. of Ti as $TiO(OH)_2$ and 100 mg. of Cb as Cb_2O_5, in HF solution, were treated separately by the process: the $TiO(OH)_2$ precipitate dissolved completely in the H_2O_2 and HCl, and of the $HCbO_3$ not more than 1 mg. remained undissolved.—The experiment was several times repeated with 300 mg. of Ti: in every case a large white precipitate, amounting to from one sixth to one third of the original quantity, remained undissolved by the H_2O_2 and HCl. When this residue was treated with fresh portions of the H_2O_2-HCl mixture a large part of it remained undissolved, but the solutions were strongly colored. When the residue was treated with 5 cc. of cold 27 n. HF it dissolved completely in 2 or 3 minutes.

In test analyses, the presence of tantalum was always detected in a mixture of 2 mg. of Ta with each of the following: 300 mg. of Ti, 300 mg. of W, 300 mg. of Sn, 400 mg. of Mo, 100 mg. of Cb; and satisfactory blanks were obtained when it was absent.—The presence of 3 mg. of columbium in mixtures was always detected, but the second test sometimes failed when the mixture contained 2 mg. of Cb.

The H_2O_2-HCl method fails when the hydrated oxides are precipitated by evaporating an HF solution with HNO_3 just to dryness. Thus in separate experiments with 2 mg. of Ta and 2 mg. of Cb, neither dissolved appreciably in the H_2O_2-HCl solution on 5 minutes' heating; also a mixture containing 5 mg. of Ta and 100 mg. of Ti as well as one containing 12 mg. of Cb and 100 mg. of Ti dissolved completely in the H_2O_2-HCl solution on heating for about 5 minutes. Similar results were obtained in experiments in which the hydrated oxides, precipitated as before by evaporation with HNO_3, were heated at 120° for 30 minutes.

100 mg. of Ta as Ta_2O_5 in HF were evaporated to fuming with 5 cc. of 18 n. H_2SO_4: there was a heavy white precipitate. To the cold mixture 2 cc. of 3 n. HCl were added drop by drop: a heavy white precipitate remained. The mixture was added to 10 cc. of 1 f. H_2O_2: a large residue remained, which did not decrease in amount on stand-

ing or on heating. The mixture was evaporated to fuming, the crucible being covered: the residue was less than that after the first evaporation to fuming. The cold mixture was poured into 5 cc. of water: there was a large precipitate. 10 cc. of 1 f. H_2O_2 were added: a large residue remained undissolved.—Similar experiments with smaller amounts of tantalum yielded the same results.—In similar experiments with columbium free from tantalum, clear or nearly clear H_2O_2 solutions were obtained.

D. 47.—Separation of Tungsten from Columbium, Tantalum, and Titanium by Fusion with Sodium Carbonate and Sulfur.—H. Rose in his early work, and Hall, *J. Am. Chem. Soc.*, **26**, 1238 (1904), recommended fusion with Na_2CO_3 and S to remove tungsten and tin completely from columbium and tantalum, and presumably also from titanium.

A mixture of 300 mg. of W and 300 mg. of Ti in HF solution was treated by the process described in C. E., D. 46: in the first "columbium" test there was a large precipitate of HgCl, which showed that at least 20 mg. of W had been carried by the titanium into the tantalum group; in the second test (after the fusion) only a slight turbidity resulted, which corresponded to much less than 1 mg. of W. The experiment was repeated with a mixture of 5 mg. of W and 300 mg. of Ti: no tungsten was found in the $(NH_4)_2S$ solution, but it was separated completely from the titanium by fusion with Na_2CO_3 and S as described in the first paragraph of the C. E. on D. 46.

Incomplete Separation of Tungsten from Titanium by Fusion with Potassium Nitrate and Carbonate.—This method of separation was recommended by Defacqz, *Compt. rend.*, **123**, 823 (1896).

A mixture of 10 mg. of W and 300 mg. of Ti, and one of 300 mg. of W and 300 mg. of Ti, in HF solution, were treated by the process described in the first paragraph of the C. E. on D. 46, except that the fusion was made for 30 minutes with a mixture of eight parts of KNO_3 and two parts of K_2CO_3 (instead of for 15 minutes with Na_2CO_3 and S); the melt was treated with water, the water was evaporated off, the residue was again treated with water, and the mixture filtered: no tungsten was found in the residue in the first experiment, but several milligrams were found in the second experiment.

TUNGSTEN AND TANTALUM GROUPS: PROCEDURES AND NOTES

P. 30, N. 1.—Volatility of Fluorides of Titanium, Tantalum, and Columbium.—See C. E., P. 3, N. 5.

P. 30, N. 2, 3.—Dissolving of Elements of the Tungsten and Tantalum Groups in Sulfuric Acid.—500 mg. of Sn as H_2SnO_3, 300 mg. of Ti as H_2TiO_3, 100 mg. of Cb as Cb_2O_5, 100 mg. of Ta as Ta_2O_5, and 500 mg. of Mo as MoO_3 were dissolved in separate experiments in 27 n. HF, 2–3 cc. of 36 n. H_2SO_4 (s. g., 1.84) were added, the solution was evaporated till it fumed strongly, and then after cooling it was poured gradually into 5 cc. of cold water: no permanent precipitate separated in any case; the Mo solution had a deep-blue color, and before dilution there were blue spots above the surface of the liquid.—The experiments with 100 mg. of Cb and with 100 mg. of Ta were repeated, but no especial care was taken to cool the H_2SO_4 upon dilution: a large white flocculent precipitate separated in each case.

100 mg. of W as Na_2WO_4 were dissolved in a little water, 1 cc. of 36 n. H_2SO_4 was added, and the mixture was evaporated to fuming: a large quantity of a heavy yellow powder separated.

As to the behavior of 4, 2, and 1 mg. of W, see C. E., D. 36.

P. 30, N. 5, 6.—Solution of Tungsten-Group Elements by Ammonium Sulfide.—500 mg. of Sn as metal, 500 mg. of Sb as $SbCl_3$, 500 mg. of As as As_2O_3, 250 mg. of W as Na_2WO_4, and 100 mg. of Mo as Na_2MoO_4, in separate experiments, were heated with 16 n. HNO_3; the mixture was evaporated to dryness; the residue was heated in a hot-closet at 120° for 20 minutes, and was then heated with 20 cc. of 6 n. $(NH_4)_2S$ reagent in a pressure-bottle in a steam-bath for 30 minutes: the residue in each experiment dissolved completely.

The experiment was repeated with a mixture of 500 mg. of Sn as $SnCl_2$ and 400 mg. of As as $NaAsO_2$: a clear solution resulted in one treatment.

The experiment was repeated with a mixture of 500 mg. of Sn, 500 mg. of PO_4, 2 mg. of W, 1 mg. of Mo, 1 mg. of Sb, and ½ mg. each of As and V: a large part of the material dissolved rapidly in the $(NH_4)_2S$, but about 1/20 of it remained undissolved; and this residue did not dissolve completely in a second treatment with 20 cc. of the $(NH_4)_2S$ reagent in the pressure-bottle. The filtrates were combined, and tested by P. 31–39: there were found 0.3 to 0.5 mg. of W, 1 mg. of Mo, 1 mg. of Sb, 0.3 mg. of As, 0.5 mg. of V, and nearly 500 mg. of Sn.

The experiment was repeated with 250 mg. of Mo as Na_2MoO_4, except that the heating in the pressure-bottle was continued for three hours: a black residue corresponding to perhaps half the molybdenum

remained undissolved. This residue was filtered out and heated with 20 cc. of fresh $(NH_4)_2S$ reagent in the pressure-bottle for 1 hour: much molybdenum still remained undissolved.

The experiment was repeated with 100 mg. of V as NH_4VO_3: there was a large black residue. This was filtered off and heated with 20 cc. of fresh $(NH_4)_2S$ reagent in a pressure-bottle for 30 minutes: a considerable residue remained. This was filtered off and heated with 20 cc. of fresh $(NH_4)_2S$ reagent: a small residue still remained. Each of the three $(NH_4)_2S$ filtrates was poured into 50 cc. of 6 n. H_2SO_4, and the relative sizes of the three V_2S_5 precipitates estimated by measuring them in a graduate after they had settled: it was calculated that 45 mg., 35 mg., and 15 mg. of V dissolved in the three successive $(NH_4)_2S$ treatments, and that 5 mg. of V were undissolved after the third treatment.

The experiment was again repeated with 100 mg. of V as NH_4VO_3: after the single treatment with $(NH_4)_2S$ there was a large jet-black residue, as before. This residue was washed once with 3 n. NH_4OH, then heated in a casserole for 10 minutes with 3 n. NH_4OH, and filtered: a very dark colloidal solution passed through the filter. This was acidified with H_2SO_4: a blue solution resulted, which was clear except for a little sulfur, and contained about 45 mg. of V (estimated by comparison with a standard $VOSO_4$ solution). The unchanged residue that remained on the filter (after washing with hot water) contained about 20 mg. of V. The original $(NH_4)_2S$ solution did not contain more than 15 mg. of V, and the remainder (20 mg.) was lost in the washings.

In three separate experiments, to 500 mg. of Sn as metal and 5 cc. of 16 n. HNO_3 were added, respectively, 500 mg. of V as Na_3VO_4, 500 mg. of W as Na_2WO_4, and 500 mg. of Mo as $(NH_4)_2MoO_4$; each mixture was evaporated to dryness, the residue was heated at 120° for 1 hour, and dissolved in HF; the solution was evaporated to fuming with 3 cc. of 36 n. H_2SO_4, cooled, and poured into 5 cc. of water; 15 n. NH_4OH was then added in excess: nothing remained undissolved in the mixture containing vanadium, there was a yellowish-white precipitate in that containing tungsten, and a greyish-blue one in that containing molybdenum. 10 cc. of cold $(NH_4)_2S$ reagent were then added: clear solutions resulted, those containing vanadium and molybdenum being deep-red.

In three separate experiments, to 300 mg. of V as Na_3VO_4, 300 mg. of W as Na_2WO_4, and 300 mg. of Mo as $(NH_4)_2MoO_4$ respectively, were added 10 cc. of water, 3 cc. of 15 n. NH_4OH, and 10 cc. of 6 n. $(NH_4)_2S$; each mixture was heated at 50–60° in a covered casserole

for 45 minutes: there was a rather small green precipitate in the vanadium experiment and the solution was yellow-brown; clear solutions resulted in the two other cases, and that containing molybdenum was deep orange-red.

100 mg. of Mo as $(NH_4)_2MoO_4$ were evaporated to fuming with 4 cc. of 18 n. H_2SO_4 and then treated as described in P. 30, 10 cc. of 6 n. $(NH_4)_2S$ being used in the pressure-bottle treatment: the solution was deep cherry-red and absolutely clear; there was no precipitate after cooling and standing 2 hours.

100 mg. of V as NH_4VO_3 were evaporated to fuming with 4 cc. of 18 n. H_2SO_4, 5 cc. of water were added, and the solution was made alkaline with 15 n. NH_4OH: the dark-green solution became brown in a few minutes but remained clear. 20 cc. of 6 n. $(NH_4)_2S$ were added: a large brown precipitate separated, and this remained after the 30-minute digestion in a pressure-bottle (P. 30). The mixture was filtered, and the precipitate washed with hot water: during the washing some of the precipitate passed through the filter as a colloidal solution; the amount of vanadium in the wash-water was estimated to be 25 mg. by adding H_2SO_4 and comparing the blue color with that of a standard $VOSO_4$ solution. The brown precipitate was then heated with 20 cc. of 3 n. NH_4OH in a casserole for 10 minutes, and the mixture filtered: a very dark colloidal solution passed through the filter. This was acidified with H_2SO_4: a greenish-yellow solution resulted, which was clear except for a little sulfur, and contained about 35 mg. of V (estimated after reduction with SO_2). The residue on the filter, after washing, was jet black, and contained about 10 mg. of V. The original $(NH_4)_2S$ solution contained only about 10 mg. of V.

P. 30, N. 6.—Separation of Tungsten and Molybdenum from Titanium by Ammonium Sulfide.—An HF solution containing 200 mg. of Ti, 2 mg. of W, 1 mg. of Mo, 0.5 mg. of V, 1 mg. of Sn, 1 mg. of Sb, and 0.5 mg. of As was treated by P. 30, 20 cc. of 6 n. $(NH_4)_2S$ being used in a single pressure-bottle treatment; the $(NH_4)_2S$ solution was analyzed for the elements of the tungsten group: there were found 0.7 mg. of W (in P. 36), 1 mg. of Mo, 0 mg. of V, 1 mg. of Sn, 1 mg. of Sb, and 0.1 mg. of As; and 0.5 mg. of W more in the second wash-water in P. 30, and 0.2 mg. more in the H_2SO_4 solution in P. 31.

As to the complete retention of 5 mg. of W by 300 mg. of Ti when the $(NH_4)_2S$ treatment was made at 50–60° in an open casserole, see C. E., D. 47.

A mixture of 20 mg. of Mo as $(NH_4)_2MoO_4$ and 100 mg. of Ti as $TiO(OH)_2$ in HCl was treated by P. 30: there was a purple crystalline residue in the concentrated H_2SO_4, but it dissolved on the addition

of 5 cc. of water. A grey precipitate formed with NH_4OH. After the digestion with 20 cc. of 6 n. $(NH_4)_2S$ the solution was deep-red and there was a large residue. After the first washing with hot water the precipitate on the filter was still reddish-yellow, but on further washing with hot water the residue became nearly white. The precipitate was treated by P. 41 and 42: it dissolved completely in the salicylate treatment; the NaOH precipitate was white. The NaOH solution was proved not to contain more than a trace of molybdenum by making it 0.5 n. in HCl and saturating it with H_2S. Therefore molybdenum is not carried by titanium into the tantalum group.

In separate experiments, two portions of 100 mg. of Ti as $TiO(OH)_2$ in HF solution, mixed with 50 mg. of Mo as $(NH_4)_2MoO_4$ and 50 mg. of Sb as $SbCl_3$, respectively, were treated by P. 30, 20 cc. of freshly prepared 6 n. $(NH_4)_2S$ being used: the precipitates of $TiO(OH)_2$ were white after being washed with hot water.—The experiments were repeated, except that a solution of $(NH_4)_2S$ was used which had been allowed to stand exposed to the light in an ordinary glass-stoppered bottle for about two weeks: the precipitate was brown in the first case and brilliant orange in the second, showing that it is necessary to use $(NH_4)_2S$ solution of the full strength.

A mixture of 50 mg. of Ti as $TiO(OH)_2$ and 50 mg. of Mo as MoO_3 in HF solution was treated by P. 30, the precipitate after the pressure-bottle treatment was washed thoroughly with hot water, and tested for Mo by the process used in detecting columbium in P. 48: the $HgCl_2$ solution was at first clear but became slightly turbid in 15 minutes, showing that far less than 1 mg. of Mo had been retained by the $TiO(OH)_2$.

The last experiment was repeated with a mixture of 100 mg. of Ti as $TiO(OH)_2$ and 100 mg. of W as Na_2WO_4 in HF solution: the $HgCl_2$ solution became slightly turbid at once.—The experiment was repeated, except that the $(NH_4)_2S$ precipitate was heated in a pressure-bottle for 15 minutes with 40 cc. of 3 n. NH_4OH: the $HgCl_2$ solution became only very slightly turbid, but this showed that a trace of tungsten had been retained by the $TiO(OH)_2$.

A mixture of 200 mg. of Mo and 400 mg. of Ti in HF solution was treated by the process described in C. E., D. 46: the $(NH_4)_2S$ precipitate still had a strong orange color after it had been washed 3 times with hot water on the filter with the aid of suction. It was returned to a casserole and heated with frequent stirring on a steam-bath with 10 cc. of 15 n. NH_4OH and 40 cc. of water; the precipitate was then filtered out and washed: it now had only a slight yellowish color. The treatment with the H_2O_2-HCl mixture was omitted; the

precipitate was dissolved in HF, and the solution evaporated with H_2SO_4, etc.: a precipitate of HgCl was obtained in the first $HgCl_2$ test (with one third of the solution), but none in the second test after the fusion with Na_2CO_3 and S.—The experiment was repeated, except that the digestion with 3 n. NH_4OH was omitted: large precipitates of HgCl were obtained in both the $HgCl_2$ tests, showing that digestion of the $(NH_4)_2S$ precipitate with 3 n. NH_4OH is much more effective in extracting molybdenum than is washing with hot water.

P. 30, N. 6.—Separation of Tungsten and Molybdenum from Columbium by Ammonium Sulfide.—A solution in 27 n. HF containing 100 mg. of Cb, 2 mg. of W, 1 mg. of Mo, 0.5 mg. of V, 1 mg. of Sn, 1 mg. of Sb, and 0.5 mg. of As was treated by P. 30, except that 20 cc. of 6 n. $(NH_4)_2S$ were used in the pressure-bottle treatment; the solution was analyzed for the elements of the tungsten group: there were found 0.2 mg. of W, 1 mg. of Mo, 0.05 mg. of V, 1 mg. of Sn, 0.5 mg. of Sb, and 0.2 mg. of As.

P. 30, N. 6.—Precipitation of Vanadium with Titanium in the Ammonium Sulfide Treatment.—A mixture of 200 mg. of Ti as $TiO(OH)_2$ and 50 mg. of V as Na_3VO_4 in HF solution was treated by P. 30: the large white precipitate that formed with NH_4OH turned greyish-black when $(NH_4)_2S$ was first added, and the final residue was greyish-yellow. At no time did the $(NH_4)_2S$ solution show a reddish color; the final filtrate was a clear straw-yellow, showing that it did not contain an appreciable amount of vanadium. To confirm this conclusion 0.6 mg. of V as Na_3VO_4 was added to half the filtrate: an intense red color formed at once.

See also the first experiment of C. E., P. 30, N. 6, page 336.

P. 30, N. 7.—Extraction of Molybdenum from Titanium Hydroxide and Behavior of Vanadium with Ammonium Hydroxide.—See C. E., P. 30, N. 6, and N. 5, 6 for experiments with 200 mg. of Mo and 400 mg. of Ti, and with 100 mg. of V.

TUNGSTEN GROUP

P. 31, N. 1.—Colors Produced by Molybdenum and Vanadium in Ammonium Sulfide.—To cold mixtures of 2 cc. of 95% H_2SO_4, 5 cc. of water, 6 cc. of 15 n. NH_4OH, and 20 cc. of $(NH_4)_2S$ were added 1 mg., 2 mg., and 5 mg. of Mo as $(NH_4)_2MoO_4$: there was with 1 mg. no change of color, with 2 mg. a barely noticeable orange color, with 5 mg. a marked orange color. These solutions were heated in a pressure-bottle for 15 minutes: the solution with 1 mg. showed a distinct orange shade when compared with $(NH_4)_2S$ solution; the solution with 5 mg. had a red color which was deeper than the orange color which it had before heating.

To the same kind of mixture ½ mg. of V as vanadate was added: a decided red color resulted. The solution was saturated with H_2S: the red color changed to a deeper violet-red color (see C. E., P. 106, N. 2).

The first experiment was repeated with 1, 2, and 5 mg. of Te as TeO_2 in HCl: the $(NH_4)_2S$ solution used had a pale-yellow color (due to sulfur), and the addition of the tellurium caused only a slight darkening. The heating had no effect.

P. 31, N. 2.—Precipitation of Tungsten, Molybdenum, and Vanadium from Ammonium Sulfide Solution by Acids.—In separate experiments 200 mg. of W as Na_2WO_4, 50 mg. of Mo as Na_2MoO_4, and 50 mg. of V as NH_4VO_3 were treated with enough 27 n. HF solution (3–5 cc.) to give a clear solution, 2 cc. of 36 n. H_2SO_4 were added, the mixture was evaporated to fuming, cooled, poured into 5 cc. of water, 6 cc. of 16 n. NH_4OH and 20 cc. of $(NH_4)_2S$ were added, and the mixture was heated in a pressure-bottle for 30 minutes, cooled, saturated with H_2S by passing in the gas for 20 minutes, let stand 60 minutes, diluted with 5 cc. of water, and dropped into 50 cc. of 6 n. H_2SO_4; the mixtures were filtered, the filtrates evaporated to dryness, the residues ignited (to expel NH_4 salts) and dissolved in a few drops of 6 n. NaOH, and the solutions tested for tungsten by adding 5 cc. of $SnCl_2$ reagent, or for molybdenum by adding 20 cc. of 0.5 n. HCl and saturating with H_2S, or for vanadium by adding 10 cc. of 6 n. $(NH_4)_2S$, saturating with H_2S, and comparing the color with standards: the results showed that 50 mg. of W, 0.1 mg. of Mo, and 3.6 mg. of V passed into the H_2SO_4 filtrate.

The above experiments were repeated except that the $(NH_4)_2S$ solutions were added to the H_2SO_4 immediately (without standing 60 min.) after saturating with H_2S: in these experiments 50 mg. of W, 0.1 mg. of Mo, and 4.0 mg. of V passed into the H_2SO_4 filtrate.

The above experiments were repeated except that the $(NH_4)_2S$ solutions were added to the H_2SO_4 solution immediately after the pressure-bottle treatment (without saturating them with H_2S): in these

experiments 50 mg. of W, 0.1 mg. of Mo, and 6.8 mg. of V passed into the H_2SO_4 filtrate.

The experiments described in the first paragraph were repeated, except that the $(NH_4)_2S$ solutions were dropped into 50 cc. of 6 n. H_2SO_4 immediately, without heating in a pressure-bottle: 50 mg. of W, 0.05 mg. of Mo, and 10 mg. of V passed into the H_2SO_4 filtrate.

The first experiments described above were repeated except that 2 mg. of W, 1 mg. of Mo, and 0.5 mg. of V were used (instead of the larger quantities), that the H_2SO_4 precipitates were dissolved in aqua regia, and the solutions after evaporating off the acid were tested for the elements in the way described: it was estimated that 1.5 mg. of W, 1 mg. of Mo, and 0.4 mg. of V were present in the H_2SO_4 precipitates.

The experiment described in the first paragraph was repeated with 200 mg. of W, except that, instead of dropping the $(NH_4)_2S$ solution into the 6 n. H_2SO_4, the acid was added gradually to the solution until it became acid: in this case less than 0.5 mg. of W was precipitated with the sulfur, all the remainder passing into the filtrate, which was yellow in color.

The last experiment was repeated with 5, 2, 1, and 0 mg. of W: the filtrates were deep-yellow, yellow, yellow, and colorless, respectively. In the first case the precipitate was found to contain 0.5 mg. of W and the filtrate the remainder.

Jannasch and Bettges, *Ber. d. chem. Ges.*, 37, 2223–26 (1904), have shown that when acid is added to an $(NH_4)_2S$ solution containing tungsten 50–91% of the tungsten remains in solution, but that the precipitation of MoS_3 in similar experiments is practically complete.

The last experiment was repeated with a mixture of 200 mg. of Mo as $(NH_4)_2MoO_4$ and 2 mg. of W as Na_2WO_4: the filtrate was colorless and gave no test for tungsten, showing that tungsten is carried down with MoS_3 when acid is added to the sulfide solution.—However, in certain test analyses, in which molybdenum and tungsten were both present, the latter was found only in the filtrate.

The last experiment was repeated with a mixture of 300 mg. of Sn and 10 mg. of W: the filtrate was found to contain only 1 mg. of W, showing that tungsten is carried down by SnS_2 when the acid is added to the sulfide solution.

100 mg. of V as Na_3VO_4 were digested with $(NH_4)_2S$ solution, the small bluish-grey precipitate that remained was filtered out, and the filtrate was acidified by adding 6 n. H_2SO_4 to it: a large brown precipitate and pale-blue filtrate resulted, showing that the vanadium had divided between precipitate and filtrate.—In the experiments of Noyes, Bray, and Spear, *J. Am. Chem. Soc.*, 30, 538 (1908), in which 25 or 50 mg. of V were taken and HCl or $HC_2H_3O_2$ was added to the

$(NH_4)_2S$ solution after it had been saturated with H_2S, about one half the vanadium remained in solution.

To find the effect of phosphate on the sulfide precipitation, a mixture of 4 mg. of W as $(NH_4)_2SO_4$ and 100 mg. of PO_4 as H_3PO_4 was treated by P. 30 and 31. The buff-colored precipitate was analyzed by P. 35 and 36: a very faint blue coloration was obtained with $SnCl_2$ and HCl, which corresponded to not more than 0.3 mg. of W. The H_2SO_4 solution was tested for tungsten by P. 40: a deep-blue color and some blue precipitate formed at once, showing that nearly all the tungsten had passed with phosphate into the H_2SO_4 solution.—See also C. E., P. 106, N. 3, 5.

The experiment was repeated with 4 mg. of Mo as $(NH_4)_2MoO_4$ and 100 mg. of PO_4 as H_3PO_4; the black precipitate was dissolved by P. 35, and the HCl solution, as well as the H_2SO_4 solution from the sulfide precipitate, tested for molybdenum by H_2S: practically all the molybdenum was found to have been precipitated as sulfide in P. 31.—The experiment was repeated with 50 mg. of Mo as $(NH_4)_2MoO_4$ and 100 mg. of PO_4 as H_3PO_4, the H_2SO_4 solution being evaporated almost to dryness and tested for Mo by P. 38: only a very slight pink color resulted, which corresponded to not more than 0.1 mg. of Mo.

P. 31, N. 3.—Color of Sulfides Precipitated from Ammonium Sulfide Solution by Acid.—A mixture of 2 cc. of 36 n. H_2SO_4, 5 cc. of water, 6 cc. of 15 n. NH_4OH, and 20 cc. of $(NH_4)_2S$ reagent was heated in a 50-cc. pressure-bottle for 30 minutes and then poured into 50 cc. of 6 n. H_2SO_4, and the mixture was stirred for 1 or 2 minutes: a fine, pale yellowish-white precipitate separated.—The experiment was repeated, except that 1 mg. of Sn was also added to the mixture: a coagulated precipitate of a much more pronounced yellow color resulted. —See also Noyes and Bray, *J. Am. Chem. Soc.*, **29**, 199 (1907).

P. 32, N. 1, 3, 4.—Effect of Ignition on the Solubility of Sulfides in Concentrated Hydrochloric Acid.—300 mg. of W as Na_2WO_4, 300 mg. of As as H_3AsO_4, 100 mg. of V as Na_3VO_4, and 50 mg. of Mo as $(NH_4)_2MoO_4$, in separate experiments, were digested with 10 cc. of $(NH_4)_2S$ reagent in a covered casserole, and added to an excess of H_2SO_4; the precipitate was sucked as dry as possible and transferred to a stoppered flask, 20 cc. of 12 n. HCl were poured over it, and the mixture was heated for 20 minutes on a steam-bath; the flask was connected by means of tubes passing through the stoppers with another flask containing a solution of $Pb(C_2H_3O_2)_2$ strongly alkaline with NaOH, and at the end of the 20 minutes the flask was removed from the steam-bath and a current of air was drawn through the liquid so as to carry the vapors above it into the $Pb(C_2H_3O_2)_2$ solution: in the cases of the tungsten, arsenic, and vanadium black pre-

cipitates estimated at 10 mg., 5 mg., and 15 mg., respectively, separated in the $Pb(C_2H_3O_2)_2$, while in the case of the molybdenum not even a darkening resulted.—For additional evidence that molybdenum sulfide precipitated from $(NH_4)_2S$ does not dissolve in 12 n. HCl, see Noyes and Bray, *J. Am. Chem. Soc.*, 29, 201 (1907).

The experiment was repeated separately with 300 mg. of W, with 100 mg. of V, and with 100 mg. of Mo, except that, before heating with HCl, the sulfides were ignited in a covered crucible heated for 10 minutes within a cylindrical clay jacket over a powerful burner, a current of H_2S being passed steadily into the crucible through a porcelain pipe passing through a hole in the cover: there was no darkening whatever in the $Pb(C_2H_3O_2)_2$ solution in any of the three cases.

The last experiment was repeated with 200 mg. of Sb and with 300 mg. of Sn: the residues in the crucible were black; in the HCl treatment all the antimony dissolved and all the tin dissolved except a small yellow residue. The experiment with the 300 mg. of Sn was repeated except that the crucible was heated without a jacket to only a low red heat: the residue was yellow, with some black particles; on treating it with HCl a large lustrous yellow residue (of SnS_2) remained.

P. 32, N. 2.—Composition of the Ignited Sulfides.—For the composition of the ignited molybdenum sulfide (MoS_2), see Mennicke, *Quantitative Untersuchungsmethoden des Molybdäns, Vanadiums, und Wolframs*, 19 (1913). For the composition of the ignited vanadium sulfide (V_2S_3), see Abegg-Auerbach, *Handbuch der anorganischen Chemie*, III, 3, 709 (1907). For the composition of the ignited tungsten sulfide (WS_2), see Roscoe and Schorlemmer, *Treatise on Chemistry*, Ed. 1923, 2, 1145.

P. 32, N. 2, 6.—Volatility of Tin, Antimony, and Arsenic Sulfides, of Tellurium, and of Sulfur on Ignition in Hydrogen Sulfide.—500 mg. of Sn, 500 mg. of Sb, and 400 mg. of As, as sulfides, in separate experiments, were ignited for 30 minutes in a current of H_2S in an ignition tube to a dull-red heat; the residue in the boat and the sublimate on the tube were separately tested in the usual way for the elements involved: there was found in the sublimate about 4 mg. of Sn, 150 mg. of Sb, and all the arsenic.

The experiment with the 500 mg. of Sb was repeated; except that the ignition was continued for an hour: in this case 250 mg. of Sb were found in the sublimate.

A mixture of 1 mg. of Sb, 1 mg. of Sn, and 1 mg. of As as sulfides was treated as in the first experiment: all the arsenic, and almost all the antimony and tin were found in the sublimate. The experiment was repeated except that the temperature during the ignition was some-

what lower: in this case all the tin remained in the boat, and nearly all the antimony was in the sublimate.

A mixture of 1 mg. of Sn, 1 mg. of Sb, and 200 mg. of W as sulfides was treated as in the first experiment: in the sublimate were found 0.7 mg. of Sn, almost all the antimony, and no tungsten.

Two mixtures each of 1 mg. of Sn, 1 mg. of Sb, and 100 mg. of Mo, as sulfides, were treated as in the first experiment: in one case ½ mg. of Sn, ½ mg. of Sb, and no molybdenum were found in the sublimate; in the other case ½ mg. of Sn and all the antimony were found in it.

100 mg. of Te as TeO_2 in HCl were treated with H_2S, the precipitate was washed and dried at 110° for 1 hour; the residue, which consisted of tellurium and sulfur (see C. E., P. 22, N. 4), was crushed to a powder, and treated by P. 32: nearly all of it sublimed, and the tellurium was deposited as a black metal-like substance which extended from close to the boat to a considerable distance from it. None of the sublimate dissolved in HCl, but all dissolved in a mixture of HNO_3 and HCl, showing that tellurium would remain with the arsenic sulfide (see Note 6, P. 32), or with the sulfide residue to be treated by P. 35–39. In the latter case it is precipitated with the molybdenum in P. 37.

P. 32, N. 6.—Action of Concentrated Hydrochloric Acid on the Sulfides of Arsenic, Antimony, and Tin, and on Tellurium.—See Noyes and Bray, *J. Am. Chem. Soc.*, **29**, 200–1 (1907).

P. 33, N. 1–3.—Separation of Antimony and Tin by Hydrogen Sulfide, and Detection of Antimony.—See Noyes and Bray, *J. Am. Chem. Soc.*, **29**, 203–4 (1907).

P. 35, N. 1.—Effect of Nitric and Hydrochloric Acids on the Sulfides of Tungsten, Molybdenum, and Vanadium.—300 mg. of W, 100 mg. of Mo, and 100 mg. of V, as ignited sulfides, in separate experiments, were heated with 8 cc. of 16 n. HNO_3 and 2 cc. of 12 n. HCl on a steam-bath: the black tungsten residue was completely converted into a yellow one within 5 minutes, and the molybdenum and vanadium sulfides were dissolved completely in 2 minutes.

The experiment was repeated with a mixture of 2 mg. of W and 100 mg. of Mo: no precipitate separated from the acid solution even on standing over night.

A mixture of 2 mg. of W as Na_2WO_4 and 100 mg. of V as NH_4VO_3 was heated on a steam-bath with 8 cc. of 16 n. HNO_3 and 4 cc. of 12 n. HCl; and the mixture was diluted and filtered: there was a yellow residue on the filter. 5 cc. of $SnCl_2$ reagent and then 12 n. HCl were poured over the filter in a casserole: the residue turned blue.

P. 35, N. 1.—Separation of Tungsten from Molybdenum and Vanadium by Dilute Hydrochloric Acid.—100 mg. of Mo, a mixture of 1 mg. of W and 100 mg. of Mo, and a mixture of 2 mg. of W and 100 mg. of Mo, as Na_2WO_4 and Na_2MoO_4, in separate experiments, were evaporated to dryness with aqua regia and then with 5 cc. of 12 n. HCl; the residue was heated with 20–30 cc. of 2 n. HCl; the mixture was filtered; and 5 cc. of $SnCl_2$ reagent and then concentrated HCl were poured on the filter in a casserole: in the first case, there was no coloration; in the second, a light-blue one; and in the third, a dark-blue one.

The experiment was repeated with 50 mg. of V as NH_4VO_3 and with a mixture of 50 mg. of V as NH_4VO_3 and 2 mg. of W as Na_2WO_4: in the first case there was no blue coloration; in the second, an intense blue color.

50 mg. of V as Na_3VO_4 and 2 mg. of W as $(NH_4)_2WO_4$ were evaporated twice just to dryness with 1 cc. of 12 n. HCl, and the residue was boiled for 1 minute with 10 cc. of 2 n. HCl: a distinct yellow precipitate remained, which when treated by P. 36 gave a test for tungsten corresponding to 2 mg. of W.—The experiment was repeated, except that HNO_3 was used throughout instead of HCl: when the residue after the evaporation with concentrated HNO_3 was treated with 10 cc. of 2 n. HNO_3, a similar yellow residue remained, which gave a similar test for tungsten; showing that vanadate, unlike phosphate or arsenate, does not dissolve H_2WO_4.

P. 36, N. 1, 2.—Behavior of Tungsten and Molybdenum with Stannous Chloride.—See Marbaker, *J. Am. Chem. Soc.*, 37, 86 (1915).

As to tungsten blue and molybdenum blue, see Abegg-Auerbach, *Handbuch*, IV, 1 (2), 821–2 and 621–9, respectively.

20 mg. of Mo as $(NH_4)_2MoO_4$ were evaporated to dryness first with a mixture of HNO_3 and HCl and then with HCl alone. To the residue were added 2 cc. of a $SnCl_2$ reagent (2 n. in $SnCl_2$ and 12 n. in HCl): a dark-blue precipitate formed at once and the solution was also deeply colored. The experiment was repeated several times, with 5 to 50 mg. of Mo, always with the same result.—Various unsuccessful attempts were made to convert this molybdenum blue into the orange solution characteristic of trivalent molybdenum, by heating the mixture obtained after the addition of water, $SnCl_2$, HCl, Na_2HPO_4, or mixtures of these: green or blue solutions were obtained but they did not become orange within an hour.

The experiment with 20 mg. of Mo was repeated except that 3 cc. of a reagent 1 n. in $SnCl_2$ and 2 n. in HCl were added, and the mixture was heated to boiling: a brown mixture resulted. 3 cc. of 12 n. HCl were added and the mixture again boiled: a clear orange solution

quickly resulted.—The last experiment was repeated with a mixture of 1 mg. of W as $(NH_4)_2SO_4$ and 20 mg. of Mo as $(NH_4)_2MoO_4$: a blue precipitate formed during the heating with concentrated HCl; the blue color was more distinct when the precipitate was collected on a filter and washed.

The last two experiments were repeated except that to the residue from the HCl evaporation NH_4OH was added and the mixture evaporated to about 0.3 cc.: on treatment with a reagent 1 n. in $SnCl_2$ and 2 n. in HCl and then with 12 n. HCl the results were the same as before.

For the effect of the presence of phosphate, see C. E., P. 40, N. 4.

P. 36, N. 2.—Effect of the Hydrochloric Acid Concentration in the Stannous Chloride Reagent on the Confirmatory Test for Tungsten.—0.5 mg. of W as Na_2WO_4 in 0.5 cc. solution absorbed in a small piece of filter paper was treated in a casserole in separate experiments with 5 cc. of various solutions as follows: (a) 2 n. in $SnCl_2$ and 12 n. in HCl, (b) 1 n. in $SnCl_2$ and 12 n. in HCl, (c) 1 n. in $SnCl_2$ and 6 n. in HCl, and (d) 1 n. in $SnCl_2$ and 2 n. in HCl: there resulted a blue coloration immediately in (a), gradually in (b), and very slowly in (c), but in (d) a dirty green color developed on standing.

The experiment with solution (d) was repeated except that after the addition of 3 cc. of $SnCl_2$ reagent the mixture was heated to boiling and an equal volume of 12 n. HCl added, and the mixture again boiled: a blue coloration appeared fairly quickly, and there was a distinct blue precipitate when the mixture cooled.—The experiments in the preceding section show that molybdenum blue would form if solution (a) were used.

P. 37, N. 1.—Precipitation of Molybdenum by Hydrogen Sulfide.—100 mg. of Mo as Na_2MoO_4 were introduced into each of three 20-cc. portions of H_2SO_4, which were 6 n., 1.5 n., and 0.3 n. respectively; and the mixtures were saturated with H_2S at room temperature: 60, 85, and 95 mg. of Mo were found in the precipitates respectively. The filtrates were then heated under pressure: 35, 12, and 1.5 mg. of Mo were thrown down, respectively.

100 mg. of Mo as Na_2MoO_4 in 160 cc. of 0.5 n. HCl solution were saturated with H_2S at room temperature and heated in a pressure-bottle on a steam-bath for 30 minutes, the mixture was filtered, one fifth of the filtrate was evaporated to dryness, and the residue was tested for molybdenum by dissolving it in 1 cc. of HCl, adding 5 cc. of water, 5 cc. of KSCN solution, and a few granules of zinc: only a very slight red coloration was observed, and this persisted only a few seconds, indicating a trace of iron rather than molybdenum.

P. 38, N. 1, 2.—Color Test for Molybdenum with Zinc and Potassium Thiocyanate.—For the evidence that the formula of the red compound is $Mo(OH)_2(SCN)_3$ see Abegg-Auerbach, *Handbuch,* IV, 1 (2), 543–4 (1921).

In separate experiments, 1, 0.5, and 0.1 mg. of Mo as Na_2MoO_4 were evaporated with a little HCl to dryness; to the residues were added 1 cc. of HCl, 5 cc. of water, 5 cc. of KSCN solution, and 0.1 g. of granulated Zn: in all the mixtures a red coloration developed fairly rapidly; in the case of 1 mg. of Mo it changed to pink and then to yellow in 40 minutes; in the case of 0.5 mg. of Mo it changed to light yellow in 30 minutes; and in the case of 0.1 mg. of Mo it was pale red at first and became colorless in 15 minutes.

The above experiment was repeated in separate experiments with 1 and 2 mg. of Fe as $FeCl_3$: the very deep-red coloration produced at first faded rather rapidly, the solution becoming nearly colorless in 5 minutes in the first case, and in 10 minutes in the second case.

The experiment was then repeated with a mixture of 1 mg. of Fe and 0.5 mg. of Mo, and another of 1 mg. of Fe and 0.1 mg. of Mo: in 5 minutes after the addition of zinc, a blood-red color and an orange-red one were observed respectively; the former slowly changed to yellow after 45 minutes while the latter became nearly colorless after 30 minutes.

2 mg. of Fe as $FeCl_3$ were treated by P. 38: a faint pink color appeared when the solution was acidified after the $Fe(OH)_3$ had been filtered off, but this faded in less than 30 seconds after 0.2 g. of Zn was added.—The experiment was repeated with a mixture of 2 mg. of Fe as $FeCl_3$ and 0.3 mg. of Mo as $(NH_4)_2MoO_4$: after the faint pink color due to iron had disappeared a pale pink color appeared which deepened to a red; after 25 minutes there was still a faint pink color.

P. 38, N. 3.—Effect of Tellurium in the Thiocyanate Test for Molybdenum.—10 mg. of Te as $TeCl_4$ were treated by P. 38: there was no color with KSCN alone, and a black finely-divided rather flocculent precipitate of tellurium formed slowly after the addition of the zinc.—The experiment was repeated except that 0.3 mg. of Mo was also present: a distinct pink color appeared before the black precipitate began to form; later nearly all the tellurium rose to the surface with the gas bubbles and thus permitted the red molybdenum color to be seen.

P. 38, N. 4.—Reduction of Quadrivalent Tellurium by Sulfurous Acid Alone and in the Presence of Iodide.—See Noyes and Bray, *J. Am. Chem. Soc.,* 29, 202–203 (1907); also C. E., P. 72, N. 3.—As to the separation of selenium from tellurium by H_2SO_3 in concentrated HCl, see Keller, *J. Am. Chem. Soc.,* 19, 771 (1897).

P. 39, N. 1.—Behavior of Quadrivalent and Quinquivalent Vanadium with Ammonium Hydroxide.—50 mg. of V as NH_4VO_3 in HCl solution were evaporated slowly to dryness, the residue was dissolved in 2 n. HCl and again evaporated to dryness: the solution turned green during the first evaporation, and the 2 n. HCl solution was blue, showing that the vanadium had been nearly completely reduced to the quadrivalent state, $VOCl_2$. The residue was treated with 10 cc. of 3 n. NH_4OH: a large brown precipitate formed, which remained on heating. The mixture was cooled and saturated with H_2S: the brown precipitate remained undissolved, and the colorless solution became red.

The experiment was repeated except that the residue after the HCl evaporation was heated with 16 n. HNO_3 and then evaporated to dryness: the residue was red. To it were added 5 cc. of 6 n. NH_4OH: a clear colorless solution resulted.

P. 39, N. 2, 3.—Colors of Vanadium and Molybdenum in Ammonium Sulfide and Hydrogen Peroxide Solutions.—See C. E., P. 106, N. 2–6.

P. 40, N. 4.—Effect of the Presence of Phosphate on the Test for Tungsten with Stannous Chloride.—In separate experiments, to 1 mg. of W and 5 mg. of W as $(NH_4)_2WO_4$ were added 50 mg. of PO_4 as H_3PO_4, 1 cc. of 18 n. H_2SO_4, and 1 cc. of 16 n. HNO_3; the mixture was evaporated to dryness. 1 cc. of 12 n. HCl was added and the mixture again evaporated to dryness. 3 cc. of a reagent 1 n. in $SnCl_2$, 2 n. in HCl were added, the mixture was boiled, 3 cc. of 12 n. HCl were added, and the mixture again boiled: a blue color developed within a few seconds, and gradually deepened on standing, but no precipitate separated in several hours.

The experiment was repeated with a mixture of 1 mg. of W as $(NH_4)_2WO_4$, 5 mg. of Mo as $(NH_4)_2MoO_4$, and 10 mg. of V as Na_3VO_4: a clear orange-red solution resulted, which acquired a blue tinge within 30 minutes, and was distinctly blue in 3 hours; showing that the presence of phosphate with molybdenum and vanadium delays the tungsten test.—The experiment was repeated except that no tungsten was added: the solution remained orange-red for over 24 hours.

A number of experiments similar to the preceding were performed, except that a $SnCl_2$ reagent 2 n. in $SnCl_2$ and 12 n. in HCl was used; and the mixture was not heated: with 20 mg. of molybdenum alone no molybdenum blue was formed (cf. C. E., P. 36, N. 1, 2), and the solution remained orange-red; with 1 mg. of W alone, a blue color appeared at once; with a mixture of 1 mg. of W, 5 mg. of Mo, and 10 mg. of V, an intense blue color appeared within 3 hours; with 1 mg. of W mixed with either Mo or V the blue color appeared within 1 hour.

TANTALUM GROUP

P. 41, N. 1.—Behavior of Tantalum and Columbium in the Salicylate Treatment.—See Hauser and Herzfeld, *Zentralbl. f. Mineralogie,* 1910, 759; Müller, *J. Am. Chem. Soc.,* 33, 1506 (1911).

1 mg. of Cb as Cb_2O_5, 1 mg. of Ta as Ta_2O_5, 100 mg. of Cb as Cb_2O_5, and 100 mg. of Ta as Ta_2O_5 were in separate experiments dissolved in 27 n. HF and treated by P. 30 and 41. In the experiments with 1 mg. of Cb and 1 mg. of Ta the boiling solutions (P. 41) had a distinctly turbid appearance, and white flocculent precipitates were seen on allowing the hot solutions to stand. In the experiments with 100 mg. of Cb and 100 mg. of Ta the precipitates were yellow.

The experiments with 100 mg. of Ta and 100 mg. of Cb were repeated with purer salicylic acid: the precipitates (P. 41) were nearly pure white (or only faintly cream colored), not yellow as in the earlier experiments.

The experiment was repeated with mixtures of 100 mg. of Ti as $TiO(OH)_2$ and 1 mg. of Cb as Cb_2O_5, and of 100 mg. of Ti as $TiO(OH)_2$ and 1 mg. of Ta as Ta_2O_5. The boiling solutions were again turbid, even after complete solution of the Ti, and the filtered precipitates gave satisfactory tests for Cb and Ta, when tested by P. 48 and 47, respectively.

2 mg. of Ta and 2 mg. of Cb as fluorides were treated in separate experiments by P. 30, except that the $(NH_4)_2S$ was replaced by NH_4OH; the precipitate was treated by P. 41, except that 20 cc. of 1 n. Na_2HPO_4 were added to the salicylate solution: there was a distinct precipitate in each case which remained after 2 hours' boiling, the precipitate in the Cb experiment was about twice as large as that in the Ta experiment. These results show that the presence of phosphate does not interfere with the precipitation of tantalum and columbium.

Behavior of Zirconium in the Salicylate Treatment.—See Dittrich and Freund, *Z. anorg. Chem.,* 56, 344 (1907).

5 mg. of Zr as $ZrO(OH)_2$ were treated by P. 41: at no time during the 2 hours' boiling did the precipitate appear to dissolve. The filtrate was treated by P. 42 and 43: no titanium was found and the amount of zirconium precipitated as phosphate (P. 43) was estimated to be 0.5 mg. That the residue from the salicylate treatment contained 4.5 mg. of Zr was proved by dissolving it in HNO_3 and precipitating the zirconium as phosphate (as in P. 43 or 49).

1 mg. of Zr as $ZrO(NO_3)_2$ was added to 400 cc. of boiling salicylate solution (15 g. of salicylic acid and 5 g. of Na_2CO_3): a white precipitate formed at once which seemed to redissolve when the hot solution was shaken; the solution on boiling seemed almost clear. 5 cc. of 6 n.

NH_4OH were added: there was no appreciable turbidity. 5 cc. of 1 n. Na_2HPO_4 were added: the solution soon became turbid and a fine-grained precipitate settled out on standing, showing that zirconium phosphate may be completely precipitated by phosphate from a solution of ammonium salicylate. In a blank experiment with the salicylic acid and Na_2CO_3 no precipitate was obtained with NH_4OH and Na_2HPO_4.

A mixture of 2 mg. of Zr and 200 mg. of Ti as hydroxides precipitated by NH_4OH was treated by P. 41, 1 mg. of V as Na_3VO_4 being added to the salicylate solution: a small residue remained after 2 hours' boiling. This residue was dissolved in a mixture of 6 n. HNO_3 and H_2O_2, and treated by P. 43: it was estimated to contain 0.5–1 mg. of Zr and 5–10 mg. of Ti.

The last experiment was repeated with 5 mg. of Zr and 200 mg. of Ti (and 1 mg. of V); the residue that remained after 2 hours' boiling was treated by P. 43: it was estimated to contain 3–5 mg. of Zr. (The salicylate solution was analyzed by P. 43 and 44: from the color with NH_4OH and H_2S the solution was estimated to contain 0.3–0.5 mg. of V.)

P. 41, N. 2.—Behavior of Titanium in the Salicylate Treatment.— For the constitution of complex compounds of quadrivalent titanium with salicylic acid and other phenolic acids see Hauser and Lewite, *Ber. d. chem. Ges.*, **45**, 2481 (1912); Rosenheim and Schnabel, *ibid.*, **38**, 2781 (1905).

100 mg. and 200 mg. of Ti as $TiO(OH)_2$ in HF, in separate experiments, were evaporated to fuming with 3 cc. of 36 n. H_2SO_4, and subjected to the $(NH_4)_2S$ pressure-bottle treatment. The precipitate was then suspended in 400 cc. of hot water containing 5 g. of Na_2CO_3 and 15 g. of salicylic acid and boiled: in 30 minutes and 60 minutes, respectively, solution was complete, the solution being perfectly clear and deep orange-red in color.

Separate mixtures of 100 mg. of Cb and 1 mg. of Ti, and of 100 mg. of Cb and 100 mg. of Ti, as oxides, were dissolved in 27 n. HF, evaporated to fuming with 36 n. H_2SO_4, and treated by P. 30 and 41. In the experiment with 100 mg. of Cb and 1 mg. of Ti, the filtrate, which had a yellow color inclining to orange, showed 0.5 mg. of Ti when tested for Ti. In the experiment with 100 mg. of Cb and 100 mg. of Ti, the precipitate was yellow; it was dissolved in 36 n. H_2SO_4, the Cb precipitated with 15 n. NH_4OH, and the precipitate treated with 10 cc. of 3% H_2O_2 and 3 cc. of 6 n. HCl and filtered: the filtrate showed a yellow color equivalent to that produced by titanium in quantity between 1 and 2 mg.

The experiment was repeated with a mixture of 100 mg. of Ta and

1 mg. of Ti, and with one of 100 mg. of Ta and 100 mg. of Ti, as oxides. In the experiment with 100 mg. of Ta and 1 mg. of Ti, the filtrate, which had a light-orange color, showed more than 0.5 mg. of Ti. In the experiment with 100 mg. of Ta and 100 mg. of Ti, the filtrate was deep-orange in color. The yellow precipitate was found to contain between 1 and 2 mg. of Ti.

A mixture of 100 mg. of Ti as $TiO(OH)_2$ in HF solution with 200 mg. of PO_4, as H_3PO_4, was treated by P. 30 and 41: a clear orange solution resulted in P. 41.

P. 41, N. 3.—Behavior of Vanadium in the Salicylate Treatment.—A residue from the $(NH_4)_2S$ treatment, which contained 200 mg. of Ti and 50 mg. of V, was treated by P. 41: within an hour the residue had dissolved completely and the solution was deep orange-red in color. The solution was divided into two equal parts.—One portion was acidified with 12.5 cc. of 6 n. H_2SO_4. The large precipitate of salicylic acid was filtered off and analyzed (see C. E., P. 42, N. 1): it contained 5–10 mg. of Ti and only about 1 mg. of V. The filtrate from the H_2SO_4 precipitate was made alkaline with NH_4OH: a large white precipitate was formed which contained nearly all the titanium and vanadium. This was proved by evaporating the NH_4OH filtrate to dryness, destroying the organic matter with fuming H_2SO_4 and HNO_3, and analyzing the residue by P. 42–44: only 0.5 mg. of Ti and about 1 mg. of V were found.

A brown residue from the $(NH_4)_2S$ treatment, which contained about 50 mg. of V, was added to 180 cc. of the salicylate solution (P. 41): it dissolved completely at room temperature, giving a dark-green solution. This solution was boiled for 2 hours: the color gradually darkened and was brown rather than green, but no precipitate formed.

Two black residues from $(NH_4)_2S$ treatments (see C. E., P. 30, N. 5, 6), which contained about 10 and 20 mg. of V, were added to about 30 cc. of the salicylate solution (P. 41): they dissolved on moderate heating to form dark-green solutions; these darkened when boiled for 2 hours, but no precipitate separated.

100 mg. of V as NH_4VO_3 were added to 100 cc. of the salicylate solution (P. 41): the solution had an intense olive-green color, which gradually darkened on heating.

P. 41, N. 3.—Behavior of Tungsten and Molybdenum in the Salicylate Treatment.—5 mg. of W as Na_2WO_4 were evaporated to dryness with HCl, the yellow residue was collected on a filter, washed, and treated with a solution of salicylic acid and Na_2CO_3 prepared as in P. 41: the H_2WO_4 dissolved in 30 cc. of this solution at 50–60° in about 5 minutes, and the faint pink color of the salicylate solution was not

changed. 200 cc. more of the salicylate solution were added, and the mixture was heated at 100° for 3 hours: the solution remained clear.

About 10 mg. of Mo as ammonium thiomolybdate (precipitated from Na_2S solution by NH_4Cl and washed with cold water) was treated by P. 41: the salicylate solution became turbid after a few minutes' boiling, and a considerable dark-orange precipitate separated in 2 hours. On concentrating the filtrate (P. 42) a little more of this precipitate separated. After acidifying, extracting the salicylic acid with ether, and saturating with H_2S, no precipitate separated.

P. 41, N. 4.—Behavior of Bismuth, Lead, Copper, and Iron Sulfides in the Salicylate Treatment.—10 mg. of Bi as freshly precipitated Bi_2S_3 were treated by P. 41: the Bi_2S_3 did not dissolve, and after 2 hours' boiling its amount appeared to be unchanged. It was filtered off and the salicylate solution treated by P. 42. After the extraction of the salicylic acid by ether the solution was neutralized with NH_4OH, made 0.3 n. in HCl, and saturated with H_2S: a small black precipitate formed, corresponding to only 0.1–0.2 mg. of Bi.

In separate experiments, 5 mg. of Pb and 5 mg. of Cu as freshly precipitated sulfides were boiled with 200 cc. of the salicylate solution: the precipitates appeared to be unchanged in amount after 2 hours' boiling.

10 mg. of Fe as $FeCl_3$ were precipitated by NH_4OH and the mixture treated with $(NH_4)_2S$ in a pressure-bottle, as in P. 30. The black residue was treated by P. 41: it slowly dissolved to give a deep-red solution, and a small black residue, corresponding to about one tenth of the original, remained after 2 hours' boiling.

To 5 g. of Na_2CO_3 and 15 g. of salicylic acid dissolved in 400 cc. of hot water were added 0.5 mg. of Fe as $FeCl_3$: a deep-pink color was produced. A further addition of 3 mg. of Fe produced a red coloration.

P. 42, N. 1.—Precipitation of Titanium Phosphate with the Salicylic Acid Precipitated by Sulfuric Acid.—A salicylate solution which contained 200 mg. of Ti and 50 mg. of V was divided into two equal parts. —To one portion were added 10 cc. of 1 n. Na_2HPO_4, and the mixture was boiled for 1 hour. The precipitate that separated was analyzed by boiling it with 2 n. NaOH, testing the residue for titanium (P. 43) and the NaOH solution for phosphate and vanadium (P. 44): it was estimated to contain 15–25 mg. of titanium, a corresponding amount of phosphate, and only about 1 mg. of vanadium. The salicylate filtrate was acidified with 12.5 cc. of 6 n. H_2SO_4, and the large precipitate filtered off; the acid solution was found to contain nearly all the vanadium but only 2–5 mg. of titanium, showing that most of the titanium had been precipitated with the salicylic acid as phosphate; this con-

clusion was confirmed by destroying the salicylic acid with fuming H_2SO_4 and HNO_3, and analyzing the residue by P. 43 and 44: large amounts of titanium and phosphate (and no vanadium) were found.—The experiment was repeated with the other half of the salicylate solution, except that Na_2HPO_4 was not added: only 5–10 mg. of Ti and 1 mg. of V were found with the salicylic acid.—These experiments prove that titanium phosphate (but not titanium vanadate) is carried down with the salicylic acid.

P. 42, N. 1.—Behavior of Titanium in the Extraction of Salicylic Acid by Ether.—2 mg. of Ti as $TiO(OH)_2$ in HCl were treated by P. 41, 42, and 43: the amount of titanium found in P. 43 was estimated to be 2 mg. The solution of salicylic acid in 60 cc. of ether, which had a yellow color, was evaporated to dryness on a water-bath; the salicylic acid was destroyed almost completely by fuming H_2SO_4 and HNO_3, 200 cc. of 16 n. HNO_3 being used; and the resulting H_2SO_4 solution was made alkaline with NaOH: a small black precipitate separated and the solution was dark-red. The precipitate was washed with hot water, and dissolved in HF; the solution was evaporated to fuming with 2 cc. of 18 n. H_2SO_4, and made alkaline with NH_4OH: a small precipitate corresponding to not more than 0.1 mg. of Ti resulted. There is, therefore, no danger of the loss of an appreciable amount of titanium in the ether-salicylic acid solution.

P. 42, N. 2.—Separation of Titanium and of Zirconium from Phosphate by Sodium Hydroxide.—In the first experiment in C. E., P. 42, N. 1, two different precipitates of titanium phosphate containing approximately 20 and 75 mg. of Ti were boiled for 3–4 minutes with 10–15 cc. of 2 n. NaOH, and as already stated much PO_4 was found in the NaOH solution. The two residues from the NaOH treatment were washed, dissolved in 6 n. HNO_3, and tested separately for PO_4: the smaller residue contained no phosphate, and the other only about 0.5 mg., showing that a single treatment of the precipitated phosphate with 2 n. NaOH effects a satisfactory separation of the titanium and phosphate.

40 mg. of Zr as precipitated phosphate (which had been left as a residue after treatment with fuming sulfuric acid and dilution with 10 cc. of water) were boiled with 5 cc. of 6 n. NaOH in a casserole for 5 minutes; the mixture, which then had a volume of 1 or 2 cc., was diluted to about 8 cc., heated to boiling, filtered, and the residue washed. The filtrate was shown to contain much phosphate by acidifying it with HNO_3 and treating it by P. 40. The residue from the NaOH treatment was digested with 6 n. HNO_3: nearly all of it dissolved, but the HNO_3 solution was found to contain no phosphate.

The small residue that remained was dissolved in HF and HNO_3, and the solution was evaporated just to dryness; the residue was dissolved in 6 n. HNO_3 and tested for phosphate: only about 1 mg. of PO_4 was found, showing that precipitated zirconium phosphate had been nearly completely decomposed by the hot concentrated NaOH solution.

The experiment was repeated with 100 mg. of Zr, except that dilute NaOH was used. The phosphate was boiled (1) for 2 minutes with 30 cc. of 1 n. NaOH; then (2), after filtering, for 2 minutes with 30 cc. of 2 n. NaOH; (3) for 10 minutes with 2 n. NaOH; and (4) for 10 minutes with 6 n. NaOH: the amounts of phosphate found in the successive NaOH solutions corresponded to about 60, 36, 4, and 0.1 mg. of Zr, respectively; showing that precipitated zirconium phosphate is rapidly decomposed by hot 1–2 n. NaOH.

P. 42, N. 2.—Separation of Titanium and Vanadium by Sodium Hydroxide.—A mixture of 100 mg. of Ti as $TiO(OH)_2$ in HF and 1 mg. of V as $NaVO_3$ was evaporated with 1 cc. of 36 n. H_2SO_4 almost to dryness in a platinum dish. The residue was taken up in 2 cc. of 3 n. HNO_3, 6 cc. of 6 n. NaOH added, and the mixture boiled for 3 minutes. 10 cc. of water were added and the solution again boiled for 3 minutes, water being added to replace that which evaporated; the mixture was filtered. The filtrate was made just acid with HCl, 2 cc. of 15 n. NH_4OH were added, and the solution was saturated with H_2S. The color produced was judged by comparison with standards to correspond to 1 mg. of vanadium.

In another experiment a mixture of 1 mg. of V and 200 mg. of Ti was treated by P. 41, 42, and 44: in the test for vanadium in P. 44 there was a color estimated to be that produced by 0.3–0.5 mg. of V.

40 mg. of Ti as $TiO(OH)_2$ in HF and 10 mg. of V as $NaVO_3$ were evaporated to fuming with 2 cc. of 36 n. H_2SO_4, the solution diluted with 10 cc. of water, made alkaline with ammonia, shaken vigorously, and filtered after five minutes. (The filtrate gave no test for vanadium with NH_4OH and H_2S.) The precipitate was dissolved in 5 cc. of HNO_3 and evaporated just to dryness, 10 cc. of 6 n. NaOH added to the residue, which was thoroughly broken up with a stirring rod, the mixture boiled for 5 minutes, and filtered through a hardened filter.—The filtrate was divided into 3 equal portions. To the first portion were added 2 cc. of 1 f. H_2O_2 and a 2-cc. excess of 6 n. HCl: the color resulting indicated the presence of considerable titanium. The second portion was diluted with an equal volume of water and boiled 5 minutes: a precipitate estimated at 1–2 mg. of Ti formed, showing that 6 n. NaOH dissolves an appreciable amount of titanium. The third portion was now again boiled for 5 minutes without diluting: no precipi-

tate formed, showing that boiling alone will not precipitate Ti completely from 6 n. NaOH.—The original NaOH precipitate was now dissolved in HNO_3, evaporated to dryness, the residue taken up in 2 cc. of 3 n. HNO_3, 6 cc. of 6 n. NaOH added, the mixture boiled for 3 minutes, 10 cc. of water added, the mixture again boiled for 3 minutes, and the precipitate filtered out. One half of this filtrate was diluted with an equal volume of water and boiled for 5 minutes: no further precipitate resulted. The solution was cooled, acidified, and 2 cc. excess HCl added with 2 cc. of H_2O_2: no color was produced, showing that titanium had been completely precipitated by 2 n. NaOH, and that no vanadium had been carried down with the titanium in the original NaOH precipitation.

P. 43, N. 1.—Delicacy of Hydrogen Peroxide Color Test for Titanium.—To 5 cc. of 6 n. HNO_3 and 1 cc. of 1 f. H_2O_2 was added 0.1 mg. of Ti as $TiCl_4$: a distinct yellow color was produced at once.

P. 43, N. 2, 3.—Separation of Zirconium from Titanium by Phosphate and Hydrogen Peroxide. Formulas of the Phosphates.—See Hillebrand, *Bull. U. S. Geol. Survey,* **176**, 75 (1900), **700**, 173 (1919). In the earlier edition Hillebrand stated that the H_2SO_4 concentration should not exceed 1% (about 0.2 n.), but in the 1919 edition 20% acid and a large excess of a soluble phosphate are recommended. The residue after ignition of the precipitate has the formula ZrP_2O_7 (46.3% ZrO_2), showing that the precipitate was an acid phosphate, such as $Zr(HPO_4)_2$ or $ZrO(H_2PO_4)_2$. Hevesy and Kimura, *J. Am. Chem. Soc.*, **47**, 2542 (1925), have analyzed it and found it to be either $Zr(HPO_4)_2 \cdot H_2O$ or $ZrO(H_2PO_4)_2$.

For evidence that the precipitation is incomplete at low concentration of Na_2HPO_4, and that there is a delay in the precipitation of 1 mg. of Zr when the H_2SO_4 concentration exceeds 1 n., see Noyes, Bray, and Spear, *J. Am. Chem. Soc.*, **30**, 559–60 (1908).

P. 43, N. 3.—Precipitation of Titanium Phosphate.—See Noyes, Bray, and Spear, *J. Am. Chem. Soc.*, **30**, 560–1 (1908).—To 1 mg. of Ti as chloride in 3 cc. of 6 n. H_2SO_4 were added 10 cc. of water and 10 cc. of 1 n. Na_2HPO_4: upon standing 10 minutes a distinct turbidity was apparent, and after 30 minutes the precipitate had settled out.—The experiment was repeated with 5 cc. (instead of 3 cc.) of 6 n. H_2SO_4. In this case the turbidity was not apparent until after 25 minutes, and the precipitate settled only after standing several hours.

P. 44, N. 2.—Effect of Ammonium Salts on the Color Test for Vanadium with Hydrogen Sulfide.—See Noyes, Bray, and Spear, *J. Am. Chem. Soc.*, **30**, 537 (1908).

P. 45, N. 2, 3.—Behavior of Tantalum, Columbium, Titanium, and Zirconium in Carbonate Fusions.—100 mg. of Ta as Ta_2O_5 in HF were evaporated to dryness with 2 cc. of 18 n. H_2SO_4, the residue was fused for 20 minutes with 5 g. of K_2CO_3, and the melt cooled and treated with 10 cc. of cold water as described in P. 45: the melt dissolved quickly, the solution was opalescent, but no residue settled out in a few minutes. By pouring it repeatedly through a filter a clear solution was obtained. The small residue on the filter was dissolved by pouring 2 cc. of 27 n. HF repeatedly through the paper, and the HF solution was evaporated to strong fuming with 3 cc. of 9 n. $HClO_4$ (P. 3); 10 cc. of water were then added and the mixture heated: a very small residue remained which was estimated to correspond to not more than 0.5 mg. of Ta.—One fourth of the K_2CO_3 solution was heated to boiling: a large precipitate formed, showing that the melt must be treated with cold water.—The remaining three fourths of the solution was clear even after 24 hours.

The experiment was repeated with 100 mg. of Ta from the salicylate treatment (P. 41); the filter was incinerated, and the organic matter destroyed as described in P. 45; the residue was fused for only 5 minutes with 2 g. of K_2CO_3, and the melt treated with 25 cc. of cold water: a solution was obtained which was only a little more opalescent than that in the preceding experiment. On standing over night, however, a precipitate settled out, which was estimated to contain about one third of the tantalum. The mixture was filtered and the remaining two thirds of the tantalum was precipitated by treating the filtrate with SO_2 by P. 46.

The last experiment was repeated with 100 mg. of Ta and 100 mg. of Cb in separate experiments, except that 2 g. of Na_2CO_3 were used instead of 2 g. of K_2CO_3: there were in the residues undissolved by 25 cc. of water a considerable quantity of Ta_2O_5 and a little Cb_2O_5, which had not been acted on by the flux. Precipitates separated when the mixtures were allowed to stand over night. The filtrates were then treated with SO_2 and estimated to contain about 10 mg. of Ta and 80 mg. of Cb, respectively.

As to the behavior of titanium in the carbonate fusion, see Meyer and Hauser, *Analyse der seltenen Erden und der Erdsäuren*, 288 (1912).

As to the separation of zirconium from phosphate by fusion with carbonate see Hillebrand, *Bull. U. S. Geol. Survey*, 700, 127 (1919); or Treadwell-Hall, *Quantitative Analysis*, 5th ed., 505 (1919).

50 mg. of Zr as precipitated phosphate on a filter were treated by P. 45, except that it was fused with 5 g. of Na_2CO_3 instead of K_2CO_3. The aqueous extract was shown to contain a large amount of phosphate by testing an aliquot part for phosphate by P. 40. The residue from

the aqueous extract was again fused with Na_2CO_3: the second aqueous extract contained only a trace of phosphate, showing that almost all the phosphate had been removed in the first fusion.

100 mg. of Zr as precipitated phosphate were evaporated to dryness with 1 cc. of 18 n. H_2SO_4 and fused with 2 g. of Na_2CO_3 for 5 minutes. The 25-cc. aqueous extract of the melt was heated on a steam-bath for 30 minutes: a small flocculent precipitate separated. A current of SO_2 was then passed into the hot solution (P. 46): nearly all the precipitate dissolved; the minute residue that remained did not dissolve when 5 cc. of 12 n. HCl were added; it was estimated to correspond to not more than 0.1 or 0.2 mg. of Ta or Cb, and was too small to be analyzed by P. 47 and 48.

A mixture of 100 mg. of Zr as precipitated phosphate and 2 mg. of tantalum-free Cb as Cb_2O_5 in HF was evaporated to dryness with 2 cc. of 18 n. H_2SO_4, fused with 2 g. of Na_2CO_3 for 5 minutes, and the melt extracted with 30 cc. of cold water. The aqueous extract was treated with SO_2 by P. 46: the precipitate obtained was estimated to contain 2 mg. of Cb. It was dissolved in 2 cc. of HF and treated by P. 48, beginning with the second paragraph: the solution after passing through the zinc reductor gave a satisfactory precipitate with $HgCl_2$.—The experiment was repeated, with the same result.

A mixture of 50 mg. of Zr as precipitated phosphate and 2 mg. of Ta as Ta_2O_5 in HF was evaporated to dryness with 2 cc. of 18 n. H_2SO_4, fused with 2 g. of Na_2CO_3 for 5 minutes, and the melt extracted with 30 cc. of cold water. The aqueous extract was evaporated to dryness first with excess HCl, and then with HNO_3; the residue was heated with 20 cc. of 1 n. HNO_3, collected on a filter, washed, and tested for tantalum by P. 47: the precipitate obtained was estimated to contain 2 mg. of Ta.

A mixture of 100 mg. of Cb as Cb_2O_5 in HF, 2 mg. of Zr as nitrate, and 100 mg. of PO_4 as H_3PO_4 was evaporated to dryness with 2 cc. of 18 n. H_2SO_4, fused with 2 g. of K_2CO_3 for 5 minutes, and extracted with 10 cc. of cold water (P. 45). The small residue was collected on a filter, washed, and fused with $K_2S_2O_7$ (P. 49): the melt dissolved completely in water, and the solution was slightly yellow, indicating that a little platinum had dissolved; the precipitate obtained on adding Na_2HPO_4 was estimated to contain 2 mg. of Zr.

P. 46, N. 1.—Precipitation of Tantalum and Columbium from Carbonate Solution by Sulfur Dioxide.—See C. E., P. 45, N. 2, 3. In the experiments with tantalum or columbium alone, in which tantalum or columbium was precipitated from a carbonate solution by SO_2, the SO_2 filtrate was made alkaline with ammonia, and boiled: no precipitate formed, showing that large amounts of tantalum or columbium are

completely precipitated in half an hour. In the two experiments with a mixture of 100 mg. of Zr and 2 mg. of Cb (free from tantalum) the hot SO_2 solution remained clear for about 10 minutes, but in 20–30 minutes precipitates estimated to contain 2 mg. of Cb were obtained.

Non-Precipitation of Tungsten, Molybdenum, and Vanadium by Sulfur Dioxide.—In three separate experiments, 10 mg. of W, as $(NH_4)_2WO_4$, 10 mg. of Mo as $(NH_4)_2MoO_4$, and 10 mg. of V as Na_3VO_4 were added to 25 cc. of water in which 2 g. of K_2CO_3 had been dissolved; SO_2 was passed into the mixture on a steam-bath, rapidly until the solution was acid and then slowly for 30 minutes: no precipitate separated. The flasks were stoppered and the solutions allowed to stand for several days: no precipitate separated.

P. 46, N. 2.—Precipitation of Tantalum and Columbium by Boiling in Acid Solution, and the Effect of Sulfur Dioxide upon it.—See Meyer and Hauser, *Die Analyse der seltenen Erden und der Erdsäuren*, 273 (1912); Weiss and Landecker, *Z. anorg. Chem.*, 64, 72–74 (1909).

5 mg. of Ta as Ta_2O_5 and 5 mg. of Cb as Cb_2O_5, in separate experiments, were evaporated to strong fuming with 2 g. of $K_2S_2O_7$ and 1 cc. of 18 n. H_2SO_4, water was added gradually; the clear solution was diluted to 20 cc., and boiled for 5 minutes: a precipitate formed which was estimated to contain 5 mg. of Ta in the first experiment and 0.5 mg. of Cb in the second. The precipitate of tantalic acid was filtered off, and the filtrate made alkaline with NH_4OH: no precipitate separated, showing that the tantalum had been completely precipitated.—To the filtrate from the columbic acid 10 cc. of Na_2HPO_4 were added: within an hour a precipitate had formed which was estimated to contain 1 mg. of Cb. This was filtered off and the filtrate made alkaline with NH_4OH: the remainder of the columbium precipitated.

A solution of 5 mg. of Cb (free from tantalum) containing H_2SO_4 and H_2O_2 was evaporated to strong fuming with 2 cc. of 18 n. H_2SO_4, and added to 5 cc. of water; and the clear solution was heated to boiling: only a very small precipitate separated. SO_2 was passed through the mixture heated on a water-bath for 5 minutes, and the SO_2 was expelled by boiling the solution: a precipitate formed during this boiling. This was filtered off, and the filtrate was made alkaline with NH_4OH: no precipitate separated; showing that the columbium had been completely precipitated in the acid solution by the SO_2 treatment and boiling.

50 mg. of Zr as nitrate were strongly fumed with 2 cc. of 18 n. H_2SO_4, and the mixture diluted to 20 cc. with water; the clear solution was heated to boiling, SO_2 was passed through it on a steam-bath for 5 minutes, and the solution was boiled until the SO_2 was expelled: no precipitate separated.

P. 47, N. 2–4.—Composition and Properties of Potassium Fluotantalate, Oxyfluotantalate, Oxyfluocolumbate, Fluotitanate, and Fluozirconate.—See Marignac, *Ann. chim. phys.* (4), **9**, 268 (1866); (4), **8**, 28, 65 (1866); and (3), **60**, 257 (1860).

P. 47, N. 2.—Volatilization of Columbium on Strong Ignition in the Tantalum Test.—11 cc. of a stock solution of Cb_2O_5 in HF, which if pure would have contained 110 mg. of Cb, were treated by P. 47, except that the platinum crucible was heated to redness: a precipitate estimated to contain 8–9 mg. of Ta was obtained, showing that the columbium was not pure. The filtrate was evaporated to fuming with 2 cc. of 18 n. H_2SO_4, diluted with 5 cc. of water, and made alkaline with NH_4OH: a small precipitate corresponding to only 0.5–1 mg. of Cb separated.—The experiment was repeated with the same result, showing that about 100 mg. of Cb had been lost by volatilization.

The experiment was repeated at once with 11 cc. of the same solution, but this time the mixture was heated only moderately, as directed in the Procedure: the same quantity of oxyfluotantalate was precipitated, but there was a large residue when the filtrate was evaporated to fuming with 2 cc. of 18 n. H_2SO_4 and added to 5 cc. of water. This dissolved rapidly when 2 cc. of 1 f. H_2O_2 were added. This solution was diluted to 9.5 cc. and used as the columbium test solution (free from tantalum). 1 cc. of this solution when made ammoniacal and heated gave a precipitate that was estimated to contain 10 mg. of Cb.

P. 47, N. 3.—Precipitation of Potassium Oxyfluotantalate.—A portion of 2 mg. of Ta as Ta_2O_5 was treated by P. 47, and two other portions of 2 mg. of Ta were treated in the same way except that the residue, after adding K_2CO_3 and evaporating, was in one case heated only till it became dry (but not enamel-white) and was in the other case heated to redness: scarcely any precipitate formed in the portion heated only to dryness, a fairly large precipitate of the usual appearance separated in that treated according to the Procedure, and a lighter, more bulky, powdery one resulted in the portion heated to redness.

1 mg. of Ta as Ta_2O_5 was treated by P. 47: in a volume of 5 cc., there was, even from the hot solution, a distinct precipitate, which on cooling and standing was seen to have a greyish-white color.—A blank was treated by P. 47. In a volume of 5 cc., the solution was perfectly clear, even after standing.

100 mg. of Cb as $HCbO_3$, precipitated from H_2SO_4 solution by 15 n. NH_4OH, were treated by P. 47: at the end a large granular precipitate separated in the cold when the volume was 1.5 cc., but this dissolved on heating; and after 1 cc. more of water was added, it remained in solution even after cooling.

The experiment was repeated with a mixture of 100 mg. of Cb as

Cb_2O_5, and 1 mg. of Ta as Ta_2O_5: at the end, when the volume was 1 cc., the large, granular precipitate separated as before, and this dissolved when 3 cc. of water were added, but there then remained a small quantity of the greyish-white precipitate characteristic of tantalum.

100 mg. of Cb as Cb_2O_5 were mixed with 1 mg. of Ta as Ta_2O_5, and treated by P. 45: in a volume of 5 cc. the solution was practically clear when hot; on standing, a small quantity of precipitate settled out, which had the characteristic appearance of $2K_2TaF_7 \cdot Ta_2O_5$.

P. 47, N. 3.—Behavior of Zirconium on Ignition with Potassium Hydrofluoride.—A mixture of 50 mg. of Zr as nitrate and 2 mg. of Ta as Ta_2O_5 in HF was treated by P. 47, except that the bottom of the crucible was heated to dull redness: in the 5 cc. of solution there separated on cooling a large white crystalline precipitate which completely obscured the tantalum test. The mixture was heated to 60–70° and filtered; the residue was treated again by P. 47: this time there resulted the characteristic tantalum precipitate, which was estimated to contain 2 mg. of Ta.

The experiment was repeated with 50 mg. of Zr as precipitated $Zr_3(PO_4)_4$ which had remained undissolved by the salicylate treatment (P. 41): as before there separated in the 5 cc. of solution a large white crystalline precipitate. This was filtered off in the cold; the filtrate was analyzed for zirconium, and found to contain 20–25 mg. of Zr; the residue was again treated by P. 47: a satisfactory blank test for tantalum was obtained; on standing over night only a small crystalline precipitate separated out, which contained 2–3 mg. of Zr.

P. 48, N. 1.—Behavior of Precipitated Columbic Acid with Dilute Acids.—In five separate experiments, 1 mg. of Cb (free from Ta), in a solution which contained H_2O_2 and H_2SO_4, was evaporated to strong fuming with 1–2 cc. of 18 n. H_2SO_4, the mixture was cooled and poured into 5 cc. of cold water.—(1) In one experiment the clear solution was made distinctly alkaline with NH_4OH, and the mixture heated to boiling; this mixture was retained for comparison with the precipitates in later experiments. (2) This experiment was repeated, the mixture was neutralized with 6 n. H_2SO_4, and 1 cc. more added: the precipitate did not dissolve, even on boiling; the size of the precipitate was the same as in (1). (3) The second experiment was repeated except that 6 n. HCl was used instead of H_2SO_4: the result was the same. (4) The third experiment was repeated, except that the mixture was kept cold while the NH_4OH was added, and was at once acidified with HCl and allowed to stand in the cold: the result was the same. (5) The second experiment was repeated, with the same result.

10 mg. of Cb (free from Ta) were treated by the first paragraph of P. 48; the precipitate of columbic acid was at once filtered off, and

the filtrate made alkaline with NH_4OH: no precipitate formed, showing that the columbium had been completely precipitated.

As to the dissolving of freshly precipitated zirconium hydroxide in dilute H_2SO_4, see C. E., P. 93, N. 1.

P. 48, N. 2, 3, 4.—Behavior of Columbium and of Titanium Solutions with Zinc and with Mercuric Chloride.—As to the reduction of columbium from the quinquivalent to the trivalent state by Zn, see Osborne, *Am. J. Sci.* (3), **30**, 333 (1885).—The colors stated in N. 2 to be given by columbium and titanium were confirmed by experiments.

1 mg. of Cb as Cb_2O_5 was dissolved in HF, 1 cc. of 36 n. H_2SO_4 added, and the mixture evaporated till the acid fumed; the solution was then treated with HCl and Zn, and tested with $HgCl_2$ by P. 48; except that unamalgamated zinc was used in the reductor, and the solution was poured through the reductor instead of being retained in it for 5 minutes: a distinct, silky, white precipitate formed immediately.

The experiment was repeated with 100 mg. of Ti, with 10 mg. of Ta, and with 100 mg. of Sn, as oxides, with 300 mg. of Zr as sulfate, and with 100 mg. of Fe as $FeCl_3$, in separate experiments: in every case the $HgCl_2$ solution remained perfectly clear.—The experiment was several times repeated with 300 mg. of Ti as H_2TiO_3 from three different commercial sources: no precipitate formed at once or for a few minutes in the $HgCl_2$ solution, but a turbidity always appeared in 15 minutes, and this increased on longer standing.

1 mg. of Cb as Cb_2O_5 in HF was treated by P. 48: a distinct precipitate formed at once in the $HgCl_2$ solution.

The experiment was repeated with 100 mg. of Ti as $TiO(OH)_2$ in HF: the $HgCl_2$ solution was perfectly clear at first, but in 30 minutes there was a slight precipitate.

Winch and Chandratreya, *Chem. News*, 124, 231 (1922), state that $TiCl_3$ is not oxidized by $HgCl_2$ in the cold.

A number of experiments were made in which the Zn used in the reductor had been so heavily amalgamated that hydrogen bubbles ceased to form in the acid amalgamating solution (8–10 minutes being required to reach this state, instead of 30 seconds): even with 2 mg. of Cb the precipitate in the $HgCl_2$ solution was so small that it could scarcely be distinguished from the blank test with HCl alone.

P. 48, N. 5.—Behavior of Molybdenum, Vanadium, and Tungsten in the Zinc Reduction Test for Columbium.—0.5 mg. of Mo as Na_2MoO_4, 0.5 mg. of V as NH_4VO_3, and 0.5 mg. of W as Na_2WO_4 were in separate experiments dissolved in HF, evaporated to fuming with H_2SO_4, and put through P. 48: unmistakable white precipitates, increasing in size in the order above given, were formed in the $HgCl_2$ solutions.

The experiment was repeated with 100 mg. of Mo as $(NH_4)_2MoO_4$,

with 100 mg. of V as Na_3VO_4, and with 4 mg. of W as Na_2WO_4, in separate experiments: a large precipitate was produced in the $HgCl_2$ solution in each case.

P. 49, N. 1.—Behavior with Acids and with Fused Bisulfate of the Residue from a Carbonate Fusion of Zirconium Phosphate.—See Hillebrand, *Bull. U. S. Geol. Survey,* 700, 174 (1919).

25 mg. of Zr as precipitated phosphate were fused with Na_2CO_3 and extracted with water as described in P. 45; the residue was digested with 6 n. and 12 n. HCl: a large residue remained. The mixture was evaporated to fuming with 2 cc. of 36 n. H_2SO_4, diluted with water, and heated on a steam-bath: a large residue still remained. The mixture was evaporated to fuming and cooled; 5 cc. of 27 n. HF were added and the mixture heated gently: the residue slowly dissolved. The mixture was evaporated to fuming, poured into 5 cc. of cold water: a clear solution resulted.

The residue from the fusion of 100 mg. of Zr as precipitated phosphate was incinerated with the filter, evaporated to fuming with 2 cc. of 18 n. H_2SO_4, digested with 27 n. HF, again evaporated to fuming, added to 10 cc. of water, and boiled: a residue of moderate size corresponding to about 10 mg. of Zr remained. The mixture was evaporated to dryness, and treated by P. 49: when the melt was treated with 10 cc. of water, the solution was slightly yellow; only a very small residue remained, which did not dissolve when 0.5 cc. of 18 n. H_2SO_4 was added and the mixture boiled; no precipitate formed when the mixture was diluted to 20 cc. and boiled; after filtering, adding H_2O_2 and Na_2HPO_4 a very large precipitate separated.

P. 49, N. 1, 2.—Behavior of Bismuth in a Bisulfate Fusion.—20 mg. of Bi as $Bi(NO_3)_3$ were fused with 3 g. of $K_2S_2O_7$ in a platinum crucible for 15 minutes; the contents of the crucible were transferred to a casserole and boiled several minutes with 20 cc. of water, and the mixture was filtered. The filtrate was saturated with H_2S: a slight darkening of the solution occurred, but no precipitate separated.—The fine white granular residue was suspended in 10 cc. of water, and this was then saturated with H_2S: the white precipitate changed immediately into a black, bulky, flocculent precipitate.

P. 49, N. 3.—Non-Precipitation of Columbium from an Acid Solution by Phosphate in the Presence of Hydrogen Peroxide.—5 mg. of tantalum-free Cb were fumed with 2 cc. of 18 n. H_2SO_4, and the mixture poured into 5 cc. of water; to the clear solution were added 2 cc. of 1 f. H_2O_2 and 5 cc. of 1 n. Na_2HPO_4, the solution was heated to boiling, and then let stand at 20° for 24 hours: it remained clear.

ANALYSIS OF THE GOLD GROUP

P. 51, N. 1.—Behavior with Stannous Chloride.—See the next page.

P. 51, N. 2, 3.—Extraction of Elements of the Gold Group with Ethyl Acetate.—As to the extraction of gold from HCl solutions by ethyl acetate, see Lehner and Kao, *J. Phys. Chem.*, **30**, 126 (1926).

Solutions containing the elements in the form of chloride (except in one case noted) and the acid shown in the following table were made up to 10 cc. with water, and were shaken with 10 cc. of ethyl acetate. The quantities present in both layers were determined, usually by precipitating with H_2S, but in the experiments to which in the last column an asterisk is attached, by testing with NaOH, KI, and NH_4Cl for mercury, or with NaOH and KI for gold; and the precipitates were compared with those obtained from known amounts of the elements.

Element	*Milligrams taken*	*Acid added*	*Milligrams found in*	
			water	*ester*
Hg	1	0.2 cc. 6 n. HCl	0.3	0.7
	1	0.4 cc. 6 n. HCl	0.7	0.3
	100	None	8	92
	100	0.5 cc. 6 n. HCl	50	50
	100[a]	0.1 cc. 6 n. HNO_3	100	0
	100	2.6 cc. 3 n. $NaNO_3$	18	82
	100	2.6 cc. 3 n. $NaNO_3$ and 0.2 cc. 6 n. HNO_3	12	88
	100	0.25 cc. 16 n. HNO_3	10	90
	100	0.5 cc. 16 n. HNO_3	15	85
	100	1.0 cc. 16 n. HNO_3	12	88
	2	1.0 cc. 16 n. HNO_3	0.2	1.8
	100	0.2 cc. 6 n. HNO_3 and 1 drop 6 n. HCl	1[c]	99*
	100[b]	0.2 cc. 6 n. HCl	1.5[c]	99
	1	0.2 cc. 6 n. HNO_3 and 1 drop 6 n. HCl	0	0.7*
	2[b]	0.2 cc. 6 n. HNO_3	0.2	1.7
Au	1	0.2 cc. 6 n. HCl	0.2	0.8*
	5	0.12 cc. 6 n. HCl	1	4*
	5	0.3 cc. 6 n. HCl	0.3	4.7*
	30	None	27	3
	30	0.5 cc. 6 n. HCl	2	28
	30[b]	0.2 cc. 6 n. HNO_3	0.5	29.5
	30[b]	1.0 cc. 6 n. HNO_3	0.5	29.5
Pt	20[b]	0.2 cc. 6 n. HNO_3	20	0
Pd	20[b]	0.2 cc. 6 n. HNO_3	19.5	0.5
	95	0.05 cc. 6 n. HCl	94	0.8[d]
	95	0.5 cc. 6 n. HCl	95	0.1
	100	0.5 cc. 6 n. HCl	99	0.8

[a] In the form of $Hg(NO_3)_2$.
[b] Evaporated to dryness twice with 6 n. HNO_3 on a steam-bath.
[c] After two extractions. [d] Ester layer was slightly brown.

P. 51, N. 1.—Behavior of Gold-Group Elements with Stannous Chloride.—To solutions of 0.1 mg. of Au, of Hg, of Pt, and of Pd, in 2.0 cc. of 0.8 n. HNO_3 in separate test-tubes, two drops of 1 n. $SnCl_2$ were added: there resulted immediately a light-purple color with the gold, a grey precipitate with the mercury, a light orange-yellow color which became deeper orange after two minutes with the platinum, and a dark-orange with the palladium.

The experiment was repeated with 0.2 mg. of each element: the results were more pronounced, in the case of the palladium a nearly black solution being produced.

P. 52, N. 1.—Extraction of Mercury and Gold from Ethyl Acetate Solutions by Aqueous Chloride Solutions.—10 cc. of ethyl acetate in which were dissolved various quantities of gold as $AuCl_3$ or of mercury as $HgCl_2$ were shaken with the quantity of the chloride solution shown in the table. The two layers were separated, and tested with NaOH and KI for gold or with H_2S for mercury. The results are shown in the last two columns.

Element	*Milligrams taken*	*Chloride solution used*	*Milligrams found in*	
			chloride layer	*ester layer*
Hg	1	Two 5-cc. portions 3 n. NH_4Cl	0.5	0
	98	10 cc. 3 n. NH_4Cl	Large	1.5
	95	10 cc. 6 n. HCl	Large	1.5
Au	1	10 cc. 6 n. HCl	0	1
	1	Two 5-cc. portions 3 n. NH_4Cl	0	1
	2.5	10 cc. 3 n. NaCl and 0.2 cc. 6 n. HNO_3	0.3	2
	30	10 cc. 3 n. NH_4Cl	0.5	Large
	30	10 cc. 6 n. HCl	0.7	Large

P. 52, N. 2.—Solubility of Ethyl Acetate in Chloride Solutions.—10 cc. of ethyl acetate were shaken with 10-cc. portions of various chloride solutions in a separating funnel; the layers were then separated, and their volumes measured. The results were as follows:

Solution taken	*Volume of ester layer*	*Volume of aqueous layer*
6 n. HCl	8.0 cc.	11.7 cc.
6 n. NaCl	10.0 cc.	10.0 cc.
3 n. NH_4Cl	9.6 cc.	10.5 cc.

P. 52, N. 3.—Coloration of Ethyl Acetate by Gold Chloride.—1.5 mg. of Au as $AuCl_3$ were required to impart a recognizable yellow color to 10 cc. of ethyl acetate contained in a 50-cc. separating funnel.

P. 53, N. 2.—Behavior of Gold, Platinum, and Palladium with Iodide in Alkaline Solution.—To the number of milligrams of these elements as chlorides shown in the following table, in the volume shown, the amounts of 1 n. KI and 6 n. NaOH indicated were added, and the resulting solution was heated just to boiling.

Element	*Milligrams taken*	*Volume in cc.*	*1 n. KI added*	*6 n. NaOH added*	*Result*
Au	10	10	0.5 cc.	0.0 cc.	No precipitate.
	3	8	0.5	0.5[a]	Purple color; small precipitate after 2 minutes.
	3	8	0.5	1.0	Large flocculent red precipitate and red color immediately.
	3	8	0.25[b]	1.0	Purple color and small precipitate.
	3	8	0.5	2.0	Purple color and small precipitate.
	3	8	1.0	1.0	Red color; no precipitate.
	0.2	5	0.5	1.5	Red color almost immediately.[c]
Pt	1	5	0.5	1.0	Yellow color, no precipitate.
	4	5	0.5	1.0	Yellow color, no precipitate.
Pd	1	5	0.5	2.0	No color, no precipitate.

[a] 0.5 cc. more of 6 n. NaOH was added, and the mixture was boiled: the precipitate increased in size.

[b] 0.25 cc. more of 1 n. KI was added, and the solution was boiled: no appreciable change resulted.

[c] 0.2 mg. of Au sometimes gave as much color as 0.5 mg., showing that the color does not afford a reliable estimate of very small quantities.

P. 54, N. 1.—Precipitation of Mercury by Iodide and Ammonium Salt in Alkaline Solution.—To four test-tubes, each containing 0.1 mg. of Hg as $HgCl_2$ in 0.5 cc. of 10% KI, 1, 2, 3, and 4 cc. of saturated NH_4Cl solution were added; 5 cc. of a 20% solution of NaOH were then added to each tube. An orange turbidity resulted in the first three tubes; but there was none in the fourth tube.—To the second tube 5 cc. more of the saturated NH_4Cl solution were added: the turbidity disappeared. To the fourth tube 5 cc. more of 20% NaOH solution were added: an orange precipitate resulted.

To 100 mg. of Hg as $HgCl_2$ in 10 cc. of 3 n. NH_4Cl were added 7.0 cc. of 6 n. NaOH: a large white precipitate appeared. Then 0.5 cc. of 1 n. KI were added: the precipitate became dark-red. The mixture was heated to boiling and filtered; the filtrate was made slightly acid, and saturated with H_2S: there was no color or precipitate.

This experiment was repeated with 0.1 mg. of Hg: a white turbidity appeared after the addition of NaOH, and a yellow flocculent precipitate after the addition of KI.

To each of five test-tubes containing 0.1 mg. of Hg in 2 cc. of saturated NH_4Cl solution the amounts of 10% KI shown below and 5 cc. of 20% NaOH solution were added, with the following results:

KI added	0.2 cc.	0.3 cc.	0.4 cc.	0.5 cc.	0.7 cc.
Turbidity	slight	slight	greater	greater	none

To the third solution 2 cc. more of 10% KI were added: the turbidity disappeared.

P. 54, N. 2.—Interference of Gold with the Iodide Test for Mercury.—To a solution of 4 mg. of Au as $AuCl_3$ in 8 cc. of 3 n. NH_4Cl and 0.5 cc. of 1 n. KI 8 cc. of 6 n. NaOH were added, and the mixture was warmed to 50–60° for 5 minutes: there was a light-brown turbidity which gradually darkened and coagulated. The mixture was acidified: the precipitate nearly all dissolved (showing that the gold had not been reduced).

P. 55, N. 1.—Formation and Decomposition of Nitrosyl Chloroplatinate.—See Treadwell-Hall, *Qualitative Analysis*, 286 (1921); also W. A. Noyes and Weber, *J. Am. Chem. Soc.*, **30**, 15 (1908).

100 mg. of Pt as $(NH_4)_2PtCl_6$ were heated 15 minutes at 80–90° with 20 cc. of 12 n. HCl and 1 cc. of 16 n. HNO_3; 0.5 cc. of 16 n. HNO_3 was added, the mixture heated 15 minutes longer, and evaporated almost to dryness; then 1 cc. of water was added and the mixture heated: a pure yellow solution resulted, and there was no odor of nitrous fumes. The solution was evaporated to dryness on a steam-bath, 1 cc. of saturated NH_4Cl solution was added, the mixture was allowed to stand two hours, and filtered: the filtrate was slightly yellow. It was acidified, diluted, and treated hot with H_2S: a precipitate containing 0.5 mg. of Pt separated.

Formation of Metallic Palladium by Overheating its Chloride, and its Redissolving by Chlorine.—10 mg. of Pd as $PdCl_2$ in 1 cc. of water were evaporated to dryness on a steam-bath, and allowed to remain there 30 minutes; 10 cc. of water were added, and the mixture was heated to about 50°: a black residue remained. Cl_2 gas was then passed into the warm solution for 10 minutes: the black residue had all dissolved, giving a deep-orange solution. The solution was then boiled: it became yellow immediately.—The experiment was repeated, except that 1 drop of 6 n. HCl was added with the 10 cc. of water: the black residue dissolved in about two thirds the time previously required.

P. 55, N. 1.—Reduction of Quadrivalent to Bivalent Palladium by Evaporation with Hydrochloric Acid.—A solution of 100 mg. of Pd as $PdCl_2$ in 0.5 cc. of 16 n. HNO_3 was evaporated almost to dryness in a casserole; 0.5 cc. of 6 n. HCl was added, and the solution was evaporated just to dryness; then 0.5 cc. of 12 n. HCl was added, and the

solution evaporated to dryness; all these evaporations being made on a steam-bath. The residue was dissolved in 1 cc. of water, and the solution acidified with 2 drops of 6 n. HCl and saturated with NH_4Cl: there was no precipitate (of $(NH_4)_2PdCl_6$).

P. 55, N. 3.—Precipitation of Platinum by Ammonium Chloride.— To 5 mg. of Pt as H_2PtCl_6 12 n. HCl was added, and the mixture was evaporated to dryness, these operations being twice repeated; then 1 cc. of water and 1 drop of 6 n. HCl were added, and the solution was saturated with NH_4Cl: the supernatant liquid was colorless.

100 mg. of Pt as pure $(NH_4)_2PtCl_6$ were ignited, the residue dissolved in HCl and HNO_3, and the solution evaporated to dryness several times with HCl. The mixture was saturated with Cl_2 and evaporated to dryness; and the residue was taken up with 1 cc. of water: a dark-brown flocculent precipitate appeared. A drop of 6 n. HCl was added: the precipitate increased slightly. 0.5 cc. of water was added: the precipitate dissolved. The solution was saturated with NH_4Cl and allowed to stand 1 hour, and the precipitate was filtered out; the filtrate was evaporated to dryness, and the residue was ignited: a small black residue remained. This was dissolved in HCl and HNO_3, the solution evaporated, diluted until the acid concentration was 1 n., and H_2S was passed in for 15 minutes while the solution was on a steam-bath: a black precipitate corresponding to about 0.3 mg. of Pt separated.

1 mg. of Pt as H_2PtCl_6 was added to 10 cc. of 3 n. NH_4Cl and allowed to stand at 25° for 30 minutes: there was no precipitate. It was allowed to stand over night: a yellow crystalline precipitate appeared. The experiment was twice repeated, using 2 mg. and 4 mg. of Pt: both solutions yielded a yellow precipitate after 15 minutes.

For a similar experiment with 100 mg. of Pt in which its solution in HCl and HNO_3 was directly evaporated, and without subsequent evaporations with HCl was precipitated with NH_4Cl, see P. 55, N. 1.

P. 55, N. 3.—Precipitation of Iridium by Ammonium Chloride.—See C. E., P. 77, N. 2, 3.

P. 55, N. 4.—Colors of Precipitates Produced by Ammonium Chloride with Mixtures of Platinum and Iridium.—1 cc. of a slightly acid solution containing in three experiments different mixtures of Pt as H_2PtCl_6 and of Ir as Na_2IrCl_6 was saturated with NH_4Cl and allowed to stand with the following results:

1 mg. of Pt and 1 mg. of Ir gave a red flocculent precipitate.
10 mg. of Pt and 1 mg. of Ir gave a red crystalline precipitate, darker than precipitated $(NH_4)_2PdCl_6$.
100 mg. of Pt and 1 mg. of Ir gave an orange crystalline precipitate, redder than powdered $K_2Cr_2O_7$.

P. 55, N. 6.—Separation of Platinum from Palladium by Ammonium Chloride.—A solution of 100 mg. of Pt as H_2PtCl_6 and 1 mg. of Pd as $PdCl_2$ in 1 cc. of 12 n. HCl was evaporated almost to dryness in a casserole on a steam-bath; 2 cc. of water were added, and the solution acidified with 2 drops of 6 n. HCl and saturated with NH_4Cl: a large precipitate of $(NH_4)_2PtCl_6$ separated. This was filtered off, and the filtrate saturated with Cl_2: there was a red precipitate corresponding to 0.6 mg. of Pd. The $(NH_4)_2PtCl_6$ precipitate was washed with 5 cc. of 3 n. NH_4Cl solution; and the washings were saturated with Cl_2 and NH_4Cl: no precipitate resulted.

As to the behavior of a large quantity of palladium alone, see C. E., P. 55, N. 1.

P. 56, N. 1.—Destruction of Ammonium Salts by Hydrochloric and Nitric Acids.—A solution of 50 mg. of NH_4Cl in 10 cc. of 12 n. HCl and 1 cc. of 16 n. HNO_3 was evaporated to dryness in a casserole on a steam-bath. A little water and a few drops of K_2HgI_4 reagent were added: only a slight yellow turbidity resulted.

100 mg. of Pt as precipitated $(NH_4)_2PtCl_6$ were heated with 25 cc. of 12 n. HCl and 1 cc. of 16 n. HNO_3 in a covered casserole on a steam-bath for about 15 minutes: action had ceased and some precipitate remained. 0.5 cc. of 16 n. HNO_3 was added, and the mixture again heated for 15 minutes: the precipitate had entirely dissolved. The solution was evaporated to dryness and 1 cc. of water was added: there was no solid residue of $(NH_4)_2PtCl_6$.

Effect of Ammonium Salts on the Precipitation of Iridium as Dioxide.—100 mg. of Pt as $(NH_4)_2PtCl_6$ and 1 mg. of $(NH_4)_2IrCl_6$ were dissolved in 25 cc. of hot water; the solution was treated with 1 cc. of 0.5 f. $NaHCO_3$, and heated to boiling; a mixture of 1 cc. of a saturated Br_2 solution with 1 cc. of 0.5 f. $NaHCO_3$ was then added: the solution became somewhat reddish in color, but this color soon faded, and neither a dark-blue color nor a dark precipitate appeared.

P. 56, N. 2, 3.—Conditions for Separating Platinum from Iridium with Sodium Hypobromite.—See Mylius and Mazzucchelli, *Z. anorg. Chem.*, 89, 14, 28 (1914).

Various amounts of Ir as H_2IrCl_6 and Pt as H_2PtCl_6 were treated in the manner and with the results shown in the table. The symbol NaBrO here refers to a mixture of equal volumes of saturated Br_2 solution and of 0.5 f. $NaHCO_3$.

Expt. no.	*Element*	*Mgs. taken*	*Treatment*	*Result*
1	Ir	0.5	Added 25 cc. of water and 0.25 cc. of 3 n. Na_2CO_3; heated to 100°; cooled, added 2 cc. of NaBrO.	Blue color slowly coagulating to black precipitate.[a]
2		0.5	Added 5 cc. of water, 1 cc. of 1 f. $NaHCO_3$, and 2 cc. of NaBrO.	No change
3		0.5	Added 5 cc. of water and 0.2 cc. of 6 n. HCl; then 0.5 f. $NaHCO_3$ until alkaline and 2 cc. of NaBrO.	No change.
4		0.5	Added 5 cc. of water and 1 cc. of 1 f. $NaHCO_3$; heated to 100°, cooled, added 2 cc. of NaBrO, heated at 100° 5 minutes.	Blue color coagulated on warming.
5		0.5	Same as in Expt. 4, except that the mixture was not cooled before adding NaBrO.	Blue color and immemediate black precipitate.
6	Pt	100	Diluted to 25 cc.; added 0.5 f. $NaHCO_3$ until alkaline; heated 5 minutes at 100°; added 2 cc. of NaBrO, heated 15 minutes at 100°.	No change.
7		50	Added 2 cc. of 6 n. HCl; evaporated till residue was acid-free, added 2.5 cc. of water and 2 cc. of 0.5 f. $NaHCO_3$, heated 5 minutes at 100°; added 1 cc. of NaBrO, heated 20 minutes at 100°.	Light yellow turbidity correspondings to 1 mg. of Pt.
8		50	Same as in Expt. 7, except 1 cc. of 1 f. NaCl was added before evaporating, and only 1 cc. of 0.5 f. $NaHCO_3$ was added.	Yellowish precipitate corresponding to 2 mg. of Pt.
9	Pt Ir	50 0.5	Evaporated till no odor of acid; added 5 cc. of water and 0.5 f. $NaHCO_3$ until alkaline; heated 3 minutes at 100°; cooled, added 2 cc. of NaBrO, heated at 100° 5 minutes.	Dark color on adding NaBrO; dark precipitate after final heating.
10	Pt Ir	100 0.5	Same as in Expt. 9.	Same, except precipitate was lighter colored[b].
11	Pt Ir	1 20	First treated as in Expt. 9, then added 2 cc. more NaBrO and heated 15 minutes; added 1 drop of 95% C_2H_5OH; heated 1 hour.	Blue color and dark blue precipitate. Precipitate incompletely coagulated[c].

[a] The filtrate in Expt. 1 was saturated with H_2S at 100°: no precipitate.

[b] This was due to presence of 1 to 2 mg. of Pt as oxide; for the precipitate was dissolved in 5 cc. of 12 n. HCl and a few drops of 16 n. HNO_3; the solution was evaporated to dryness, the residue dissolved in 1 cc. of water, and the solution saturated with NH_4Cl: a dark-red precipitate formed.

[c] The filtrate in Expt. 11 was acidified with HCl and evaporated to dryness; the residue was dissolved in 1 cc. of water and the solution saturated with NH_4Cl: a yellow precipitate of $(NH_4)_2PtCl_6$ resulted.

P. 57, N. 1.—Precipitation of Palladium by Ammonium Chloride and Chlorine.—To separate 2-cc. portions of water were added 1 mg. and 0.5 mg. of Pd as $PdCl_2$, and the solutions were saturated with NH_4Cl and Cl_2; an orange-red crystalline precipitate formed in each case.

P. 57, N. 2.—Color of Rhodium Chloride Solution.—1 mg. of Rh as $RhCl_3$ was added to 2 cc. of solution saturated with NH_4Cl and Cl_2: it gave an orange color, which became orange-red on boiling.

ANALYSIS OF THE THALLIUM GROUP

P. 61, N. 3.—Precipitation of Thallium as Thallous Bromide.—To 0.5-mg. portions of Tl as $TlNO_3$ in each of several test-tubes were added 2 cc. of 9 n. $HClO_4$, 10 cc. of 12 n. $HCHO_2$, and various quantities of bromine-free HBr, NH_4Br, and NaBr as shown below; then the mixtures were cooled under a water tap and occasionally shaken: the results were as follows:

1 cc. of 1 n. HBr gave a small precipitate after 10 min.
2 cc. of 1 n. HBr gave a somewhat larger precipitate after 2 min.
2 cc. of 2 n. HBr gave a still larger precipitate immediately.
1 cc. of 6 n. NH_4Br gave this same result.
1 cc. of 6 n. NaBr gave this same result.

The third HBr experiment was repeated with the commercial acid that had not been freed from Br_2 by boiling with $HCHO_2$: no precipitate resulted.—The mixture obtained with the 2 cc. of 2 n. bromine-free HBr was filtered, and the filtrate was treated with 2 cc. of 2 n. iodine-free HI, cooled, and occasionally shaken: a slight yellow turbidity appeared after some minutes, and a very small precipitate settled out after several hours.

To 10 mg. of Tl as $TlNO_3$ were added 3 cc. of 9 n. $HClO_4$, 10 cc. of 12 n. $HCHO_2$, and 1 cc. of 6 n. NaBr; the mixture was cooled under a water tap, and occasionally shaken for 5 min.: a curdy white precipitate formed. The mixture was filtered, and to the filtrate 2 cc. of 2 n. iodine-free HI were added: a slight yellow turbidity appeared after several minutes, and a small yellow precipitate settled out after several hours.

Reduction of Trivalent Thallium by Formic Acid, and Precipitation of Thallium as Thallous Bromide.—See C. E., P. 6, N. 7–8, 10.

To 1 mg. and to 100 mg. of Tl as $TlNO_3$ 3 drops of liquid Br_2 and 3 cc. of 9 n. $HClO_4$ were added, and the mixtures were fumed; 1-cc. portions of 16 n. HNO_3 were added, and the mixtures were fumed strongly; then 10-cc. portions of 12 n. $HCHO_2$ were added, and the mixtures boiled 15 min. with a return condenser: clear solutions resulted. To each solution was added 1 cc. of 6 n. NaBr, and the mixtures were cooled and shaken 5 min.: a light-yellow precipitate formed in both cases. The mixtures were filtered, SO_2 gas was passed into the filtrates, 1 cc. more of 6 n. NaBr was added to each, and the mixtures were cooled and occasionally shaken for 5 min.: no further precipitate resulted.

P. 61, N. 3.—Precipitation of Lead and Bismuth by Hydrobromic Acid.—To 15 mg. of Pb as $Pb(NO_3)_2$ 3 cc. of 9 n. $HClO_4$ were added,

and the mixture was strongly fumed; 10 cc. of 12 n. $HCHO_2$ and 2 cc. of 2 n. bromine-free HBr were added, then the mixture was cooled and occasionally shaken for a period of 5 min.: a considerable quantity of a white crystalline precipitate separated. The mixture was filtered and washed slowly and carefully with 10 cc. of cold 1 n. bromine-free HBr: substantially all of the precipitate dissolved.

3 cc. of 9 n. $HClO_4$ were added to 300 mg. of Bi as $Bi(NO_3)_3$, and the mixture was heated to fuming. Then 10 cc. of 12 n. $HCHO_2$ and 2 cc. of 2 n. HBr were added, and the solution was cooled and shaken for several minutes: a moderate amount of light-yellow crystalline precipitate slowly formed. The mixture was then filtered, and the precipitate was washed slowly with 10 cc. of 1 n. bromine-free HBr: it completely dissolved fairly rapidly. The experiment was repeated, using 500 mg. of Bi in place of 300 mg.: a much larger precipitate came down when the HBr was added; but this precipitate was nearly all dissolved by the washing with 10 cc. of 1 n. HBr.

P. 62, N. 1.—Behavior of Lead, Thallium, and Bismuth Bromides on Treatment with Hot Water and Bromine Solution.—300 mg. of Pb were precipitated as $PbBr_2$, and the precipitate was filtered and washed with a little cold water; a 15-cc. portion of boiling water was poured through the filter four times (when no more of the precipitate seemed to be dissolving): about five sixths of the $PbBr_2$ dissolved.

100 mg. of Tl were precipitated with an excess of 6 n. NaBr, the precipitate was filtered and washed, and a 15-cc. portion of saturated Br_2 solution was poured through the filter five times: the TlBr all dissolved.

To 500 mg. of Bi as $Bi(ClO_4)_3$ in 2 cc. of 9 n. $HClO_4$ and 10 cc. of 12 n. $HCHO_2$ were added 2 cc. of 2 n. bromine-free HBr: a light-yellow crystalline precipitate separated after the solution had been cooled and occasionally shaken for several minutes. The mixture was filtered, and the residue was washed slowly with 10 cc. of 2 n. bromine-free HBr: nearly all the precipitate dissolved. A 15-cc. portion of boiling water was then poured through the filter several times: the first time a fine-grained white crystalline precipitate formed in the filtrate, but after the water had been poured through four times it all remained on the filter.

P. 62, N. 2.—Solubility of Silver Bromide in Ammonium Hydroxide.—100 mg. of Ag were precipitated with an excess of 2 n. HBr, and the precipitate was filtered out, washed, and transferred to a casserole; 10 cc. of 15 n. NH_4OH were poured over it, and the mixture was warmed and stirred for 5 minutes: only about 10 mg. of Ag remained undissolved.

P. 63, N. 2.—Precipitation of Thallium as Thallous Iodide.—See C. E., P. 61, N. 3; and Noyes, Bray, and Spear, *J. Am. Chem. Soc.*, **30**, 561 (1908).

To 0.1 mg. of Tl were added 2 cc. of 6 n. H_2SO_4 and 10 cc. of water, and SO_2 gas passed into the solution until it smelled strongly of it; 1 cc. of 1 n. KI was then added: a fine yellow precipitate separated immediately.

Into 25 cc. of water containing 1 cc. of 1 n. KI and 1 cc. of 6 n. H_2SO_4 a current of SO_2 gas was passed: the solution became yellow, the color gradually increasing in intensity, showing that a yellow coloration affords no evidence of thallium.

1 mg. of Tl was treated with a few drops of saturated Br_2 solution, the excess of Br_2 was expelled by boiling, and 500 mg. of Pb as $PbBr_2$ in 30 cc. of boiling water were added; then 6 n. $(NH_4)_2CO_3$ reagent was added until the mixture smelled strongly of NH_3, and the mixture was boiled; the large white precipitate that separated was filtered off and was treated with 10 cc. of hot 6 n. $HC_2H_3O_2$: it all dissolved. To the solution 2 cc. of 6 n. H_2SO_4 were added, the precipitate was filtered off, SO_2 gas was passed into the filtrate, and 1 cc. of 1 n. KI was added: a small yellow precipitate separated immediately.

0.5 mg. of Tl in a solution of 3 cc. of 9 n. $HClO_4$ and 10 cc. of $HCHO_2$ was treated with 1 cc. of 6 n. NH_4Br and the precipitate was filtered off, washed with 10 cc. of 1 n. NH_4Br solution, and dissolved in Br_2 solution. The solution was boiled, 6 n. $(NH_4)_2CO_3$ reagent was added until the mixture smelled of NH_3, and the mixture was heated to boiling. The small dark-red precipitate of $Tl(OH)_3$ was filtered off, washed with hot water, and dissolved in 6 n. $HC_2H_3O_2$. The solution was treated as described in the last sentence of the preceding paragraph: a small yellow precipitate separated immediately on adding the H_2SO_3 and KI.

P. 63, N. 3.—Behavior of Bismuth with Potassium Iodide.—To 1 mg. of Bi were added 2 cc. of 6 n. H_2SO_4 and 10 cc. of dilute H_2SO_3 solution; then one drop of 1 n. KI was added: a small black precipitate formed. More KI was added: an orange-colored solution resulted.

ANALYSIS OF TELLURIUM AND COPPER GROUPS

PRECIPITATION BY HYDROGEN SULFIDE

P. 70, N. 1.—Removal of Formic and Hydrobromic Acids by Evaporation with Perchloric Acid to Slight Fuming.—4.3 g. of 9 n. $HClO_4$ were weighed out in a small dish, 10 cc. of 12 n. $HCHO_2$ and 1 cc. of 9 n. HBr were added, the mixture was evaporated slowly over a small flame till, on removing the dish from the flame, there was rapid bubbling but only slight fumes of $HClO_4$, and the dish was reweighed: the residual liquid consisted of 4.0 g. (showing that the $HCHO_2$ and HBr had been mostly or entirely expelled). To 0.1 cc. of this liquid, water and 1 n. $AgNO_3$ were added: no precipitate formed (showing complete removal of the HBr).

P. 70, N. 2.—Use of Methyl Violet for Determining Hydrogen-Ion Concentrations.—See Stieglitz, *Qualitative Chemical Analysis,* **2**, 31, 61, 102 (1916); Bray and Latimer, *Course in General Chemistry,* 47 (1923).

Into each of several porcelain crucibles was measured 1 cc. of a methyl violet reagent containing 1 mg. of crystalline methyl violet in 25 cc. of 95% C_2H_5OH and 75 cc. of water; and the volumes of 1.0 n. $HClO_4$ shown below were added from a dropper. The colors produced were: blue with 0.10 cc., light-blue with 0.13 cc., blue-green with 0.16 cc. and with 0.18 cc., and green with 0.21 cc.

P. 70, N. 4.—Effect of Elements Forming Colored Salts on the Color of Methyl Violet.—To solutions consisting of 1 cc. of methyl violet reagent and 6 drops of 1.0 n. $HClO_4$ in porcelain crucibles were added such quantities of various elements as nitrates as would correspond to the presence of 500 mg. of the elements in 28 cc. of solution (the volume prevailing in P. 70 when the solution is tested). The colors of the resulting mixtures with various elements added were as follows:

None added...Blue-green.
Cobalt .....Lead-grey.
Chromium ...Very dark-green.
Copper .....Blue-green.
Nickel .....Green, like that caused by 1 drop more of 1 n. $HClO_4$.
Uranium ....Green, like that caused by 0.7 drop more of 1 n. $HClO_4$.
Ferric Iron...Green, like that caused by 2 drops more of 1 n. $HClO_4$.

Effect of Hydrobromic and Formic Acids on the Color of Methyl Violet.—1 cc. of methyl violet reagent was placed in each of two porcelain crucibles; to one were added 6 drops of pure 1 n. $HClO_4$, and to the other 6 drops of 1 n. $HClO_4$ which was also 1 n. in $HCHO_2$ and 0.1 n. in NH_4Br: the color was the same in the two cases.

P. 71, N. 2.—Effect of the Presence of Chloride on the Precipitation of Iridium by Hydrogen Sulfide.—In C. E., P. 71, N. 5, 9, 10, contrast the slight precipitation of iridium from 1 n. $HClO_4$ free from chloride with the more complete precipitation from HCl solution or from $HClO_4$ solution in the presence of NH_4Cl.

P. 71, N. 5.—Precipitation of Copper-Group Elements by Hydrogen Sulfide.—See Noyes and Bray, *J. Am. Chem. Soc.*, 29, 188 (1907), many of whose results are reproduced here.

Various quantities of these elements in solutions of various HCl or HNO_3 concentrations were treated with H_2S at 20° and allowed to stand 15 minutes with the results shown in the following table. (The experiments in HNO_3 solution are reproduced from the article of Wada and Ato, *Sci. Papers Inst. Phys. Chem. Research*, 1, 63. 1922.)

Element	*Milligrams taken*	*Cc. of solution*	*Normality*		*Precipitate*
			HCl	*HNO_3*	
Pb	10	100	0.45	—	Yes[a]
	1	100	0.3	—	Yes[b]
	2	50	0.6	—	No
	2	100	0.3	—	Yes
	300	50	—	0.6	Complete
	500	100	—	0.6	Complete
Cd	10	100	0.45	—	Yes[a]
	1	100	0.3	—	Yes
	2	16	1.8	—	No
	2	50	0.6	—	Yes
	300	50	—	0.6	Note [c]
	500	100	—	0.6	Note [c]
Bi	2	8	3.5	—	No
	2	16	1.8	—	Yes
	300	50	—	0.6	Complete
Cu	2	2	12	—	No
	2	4	7	—	Yes

[a] A precipitate appeared after 15 minutes, but was not visible at first.

[b] Scarcely visible till collected on a filter; filtrate with $(NH_4)_2S$ showed only 0.1–0.2 mg. of Pb.

[c] The precipitation was not complete after 15 minutes, but became so on long standing.

The above-given experiments with 2 mg. of copper-group elements, and entirely similar ones with As^{III}, Hg^{II}, Sb, Sn^{II}, and Sn^{IV}, are here presented in a different form. Starting with 2 mg. dissolved in 4 cc. of 7 n. HCl, precipitation occurred, upon saturating with H_2S at 20° for 15 minutes, only after adding the following quantities of water:

Water added in all.....	None	4 cc.	12 cc.	44 cc.	96 cc.
Elements precipitated ..	As^{III}, Hg^{II}, Cu	Sb	Bi, Sn^{IV}	Cd	Pb, Sn^{II}

P. 71, N. 5.—Precipitation of Tellurium Sulfide by Hydrogen Sulfide, and its Decomposition into Tellurium and Sulfur.—See C. E., P. 22, N. 4, and P. 32, N. 2, 6.

P. 71, N. 6.—Behavior of Elements of the Aluminum, Nickel, and Zirconium Groups with Hydrogen Sulfide.—Various quantities of these elements in solutions of various HCl concentrations were treated with H_2S with the results shown in the following table. The experiments with indium are taken from the publication of Wada and Ato (see C. E., P. 71, N. 5).

Element	*Milligrams taken*	*Cc. of solution*	*Normality in HCl*	*Saturation*		*Precipitate*
				temp.	*min.*	
Zn	500	100	0.30	20	5	None
	"	"	0.18	20	5	None
	"	"	0.14	20	5	None
	"	"	0.14	20	10	Yes
	"	"	0.075	20	10	Yes
	"	"	0.30	90	5	None
	"	"	0.18	90	5	Slight
	"	"	0.14	90	5	Large
	50	"	0.15	20	10	None
	"	"	0.075	20	10	Yes
Ni	500	"	0.075	20	10	None
Co	500	"	0.075	20	10	None
Fe[II]	500	"	0.075	20	10	None
Mn	500	"	0.075	20	10	None
Fe[II], Ni, Co, Mn	Mixture of 500 of each	"	0.03	20	10	1.2 mg.[a]
In	100	100	0.3	20	10	None
	10	10	"	90	10	None
	10	10	0.15	20	10	Nearly all
Ga	20	10	3.0	100[b]	30	None
	"	30	1.0	100[b]	30	None
	"	45	0.0[c]	100[b]	30	None
Zr	100	100	0.35	100[b]	60	None
Ti	100	"	0.35	"	30	Large
	"	"	0.70	"	30	None
	"	"	0.70	"	60	Turbid
	"	"	0.83	"	120	None

[a] Determined by igniting the dark precipitate (consisting mainly of sulfur) and weighing the residue.

[b] Saturated cold with H_2S and heated under pressure in boiling water.

[c] 0.66 n. in $HC_2H_3O_2$ and 0.33 n. in $NH_4C_2H_3O_2$.

P. 71, N. 6.—Co-Precipitation of Zinc, Manganese, Cobalt, Nickel, and Iron with Sulfides of the Copper Group.—500 mg. of a copper-group element and 1 mg. (or more in a few cases) of an element of the

aluminum or nickel group were together dissolved in 100 cc. of 0.3 n. HCl, the solution was saturated with H_2S in the cold, the mixture filtered, and the filtrate made alkaline with NH_4OH and saturated with H_2S. The resulting precipitates were estimated by comparison with those obtained with known quantities. The quantities of the aluminum-group or nickel-group element that were thus found to have passed into the filtrate from the first H_2S precipitate are shown in the following table.

Copper-group element	*Zinc*		*Manganese*		*Cobalt*		*Nickel*		*Ferrous iron*	
	taken	*found*	*taken*	*found*	*taken*	*found*	*taken*	*found*	*taken*	*found*
500 Cu.....	1.0	1.0	1.0	1.0	1.0	0.5	1.0	0.5	1.0	1.0
500 Pb.....	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.5	1.0	1.0
500 Cd...	1.0	0.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
" "	2.0	0.5	—	—	—	—	—	—	—	—
" "	3.0	1.0	—	—	—	—	—	—	—	—
" "	4.0	1.5	—	—	—	—	—	—	—	—

A mixture of 500 mg. of Cu with 1 mg. of Fe and 1 mg. of Ni, and a mixture of 500 mg. of Cu with 1 mg. of Co, in 40 cc. of 0.7 n. HCl, were treated with H_2S at 80° for 10 minutes, the solutions were cooled, diluted to 100 cc., treated with H_2S for 15–30 minutes, and filtered; and the filtrates were tested for iron, nickel, and cobalt: conclusive tests were obtained for all of them.

Co-Precipitation of Gallium with Elements Precipitated by Hydrogen Sulfide.—De Boisbaudran, *Compt. rend.*, **94**, 1229, 1440, 1625 (1882).

To 25 mg. of Ga as $GaCl_3$ in 30 cc. of a solution 1 n. in HCl and 0.3 n. in NH_4Cl were added in separate experiments 300 mg. of Cu, of Bi, and of Cd, as nitrates, and 300 mg. of As as $NaAsO_2$; the solutions were saturated at 90° with H_2S, cooled, diluted to 100 cc., resaturated with H_2S, and filtered; and the precipitates were analyzed for gallium by dissolving them in HNO_3, evaporating, and precipitating the gallium by boiling with $NH_4C_2H_3O_2$ and $HC_2H_3O_2$ under proper conditions (see N. 3, P. 94): there was found no gallium in the cadmium or bismuth precipitate, 0.4 mg. in the copper precipitate, and 0.6 mg. in the arsenic precipitate.

These four experiments were repeated with 2 mg. of Ga, except that the filtrates, instead of the precipitates, were tested for gallium by boiling out the H_2S, neutralizing with KOH, adding 1 cc. of 6 n. HCl and 6 cc. of 3 n. $NH_4C_2H_3O_2$, and boiling two minutes: about 2 mg. of Ga were precipitated in each case. That these precipitates were gallium was confirmed by dissolving them in 5 cc. of 6 n. HCl and adding 5 cc. of 1 n. $K_4Fe(CN)_6$: the characteristic gallium precipitate formed.

These last experiments were repeated with 2 mg. of Ga, using in separate cases 300 mg. of Hg as $Hg(NO_3)_2$, of Sb as $SbCl_3$, and of Sn as $SnCl_2$, in place of the copper-group element: the whole of the gallium (about 2 mg.) was found in the H_2S filtrate in each case.

Co-Precipitation of Indium with Elements Precipitated by Hydrogen Sulfide.—For an extended series of careful experiments on this subject see Wada and Ato, *Sci. Papers Inst. Phys. Chem. Research*, 1, 58, 64 (1922). Some of their more significant results are here tabulated. The mixtures were saturatd with H_2S at 20°.

Milligrams taken		*Cc. of solution*	*Normality in*		*Milligrams of indium in*	
Indium	*Other element*		*HCl*	*HNO_3*	*precipitate*	*filtrate*
10	20 Cu	10	0.3	—	2	8
10	20 Cu	100	"	—	0.2	9.8
5	150 Pb 150 Cd	100	—	0.3	1.5	3.5
5	150 Pb 150 Cd	50	—	0.6	0.5	4.5
1	300 Pb	50	—	0.6	0.2	0.8
1	300 Cu	"	—	"	0.2	0.8
1	300 Cd	"	—	"	0.0	1.0
1	300 Bi	"	—	"	0.0	1.0
50	300 Pb	50	—	0.6	2	48
50	300 Cu	"	—	"	7	43
50	300 Cd	"	—	"	3	47
50	300 Bi	"	—	"	2	48

P. 71, N. 5, 9, 10.—Precipitation of Molybdenum, Iridium, and Rhodium by Hydrogen Sulfide.—Various quantities of these elements were treated with H_2S in the manner and with the results shown in the following table. In the experiments where $HClO_4$ is present, a solution of the element in this acid (usually 5 cc. of 9 n.) was first fumed down to 3 cc.; HNO_3 being also present in the two cases where no HCl or NH_4Cl was subsequently added. Saturation at 90° means that the solution was heated on a steam-bath or in boiling water and that a slow current of H_2S was passed through it for the time stated. In the "heating under pressure" the mixture was filtered after the saturation at 90° in an open vessel, saturated with H_2S in the cold, placed in a tightly closed bottle, and heated in boiling water for the time shown. Where two heatings are indicated, the mixture was filtered in between, and the filtrate resaturated in the cold with H_2S before reheating under pressure. The number of milligrams of iridium in the filtrate from the last precipitation was determined (except in the first experiment with 100 mg.) by evaporating it till the $HClO_4$ fumed, diluting with 9 n. $HClO_4$, matching the purple color with standards prepared in the same way.

Element	Mgs. taken	Cc. of solution	Normal in HCl	Normal in other substances	Saturation		Precipitate	Heating under pressure				Mgs. in filtrate
					temp.	min.		hours	ppt.	hours	ppt.	
Mo	100	100	0.3	—	20°	10	Small	—	—	—	—	—
	100	100	0.3	—	90	10	Large	1	10	—	—	—
	500	110	0.65	—	90	5	Large	1	Large	3	0	4
	300	34	—	1 n. in $HClO_4$ 0.4 n. in NH_4Cl 0.15 f. in PO_4	90	10	Large	—	—	—	—	Deep blue[d]
Ir	50	100	0.3	—	20	—	< 1	—	—	—	—	—
(as $IrCl_4$)	50	100	0.3	—	90	—	Large	1	10	—	—	—
	100	110	0.65	—	90	5	Large	1	Large	3	0	> 2
	10	10	2	—	90	30	9	—	—	—	—	1
	10	10	6	—	90	30	9	—	—	—	—	1
	50	30	—	1 n. in $HClO_4$ 0.4 n. in NH_4Cl	90	15	10	2	10	4[a]	25	3
	10	10	4	3 n. in $HClO_4$	90	10	3	2	6	—	—	1
	50	18	4	1.5 n. in $HClO_4$ 0.7 n. in NH_4Cl	20	10	Note *c*	2	25	2 2[b]	10 5	10
	100	30	0	1 n. in $HClO_4$	20	10	Very small[e]	2	Medium	6[e]	Small	>50
Rh	100	30	0	1 n. in $HClO_4$	20	10	Large[e]	1	Large	1	0	0
(as $RhCl_3$)	50	34	—	1 n. in $HClO_4$ 0.4 n. in NH_4Cl	90	15	Large	—	—	—	—	0.5

[a] Before this treatment 20 cc. of 12 n. HCl were added.

[b] This was a further treatment, subsequent to the one recorded above it.

[c] Not filtered and not heated at 90° before the pressure-bottle treatment.

[d] On diluting this filtrate to 100 cc., saturating it cold with H_2S, and letting it stand over night, 50 mg. of Mo more precipitated; on boiling the filtrate from this down to 15 cc., 2 mg. more precipitated and the solution became colorless.

[e] Three 2-hour heatings with filtration and saturation in between.

A solution containing 50 mg. of Ir as $IrCl_4$, 4 cc. of 9 n. $HClO_4$, and 1 cc. of 16 n. HNO_3 was heated to strong fuming: the resulting solution was deep-purple. It was refluxed for 15 minutes with 10 cc. of 12 n. $HCHO_2$: the color changed to green, but no metal separated. 2 cc. of 9 n. HBr were added, and the solution was evaporated on a water-bath till the $HClO_4$ was almost fuming: the purple color reappeared. The solution was treated with 25 cc. of water and 4 cc. of 3 n. NH_4Cl, and was then treated with H_2S for 10 minutes in a test-tube immersed in boiling water: the solution became colorless and a small brown precipitate containing 1–2 mg. of Ir resulted. The mixture was diluted to 100 cc., and saturated cold with H_2S: no more precipitate formed. The mixture was filtered, the filtrate was evaporated nearly to fuming, 6 cc. of 12 n. HCl added, and the resulting solution saturated with H_2S and heated 30 minutes in a pressure-bottle immersed in boiling water: a brown precipitate containing 12 mg. of Ir resulted. The mixture was filtered, resaturated with H_2S and heated as just stated: a precipitate containing 6 mg. of Ir separated. The filtrate was again saturated with H_2S, and heated as before for 4 hours: there was a precipitate containing 10 mg. of Ir. The filtrate was evaporated, and its purple color compared with standards: it was estimated to contain 20 mg. of Ir. (This color comparison was also used for estimating the iridium-content of the precipitates obtained previously in this experiment and of those obtained in the following experiment.)

A solution of 50 mg. of Ir as $IrCl_4$ in 3.5 cc. of 9 n. $HClO_4$ and 1 cc. of 16 n. HNO_3 was heated till the mixture fumed strongly; 10 cc. of 12 n. $HCHO_2$ were added, and the mixture was refluxed for 15 minutes: the solution became olive-green. It was then evaporated till the $HCHO_2$ was entirely expelled: the solution was purple. To this were added 10 cc. of 6 n. HCl, and the mixture was refluxed for about 30 minutes: the color changed rapidly for 5 minutes, after which it had become a dark orange-red (dark-yellow in ½ cm. thickness, very dark-red in 3–4 cm. thickness). This solution was saturated with H_2S and heated 1¼ hours in a pressure-bottle in boiling water: a large brown precipitate resulted. The mixture was filtered and the filtrate was examined for iridium: it contained only 5 mg. of Ir.

A mixture containing 300 mg. of Mo as $(NH_4)_2MoO_4$, 5 cc. of 9 n. $HClO_4$, 1 cc. of 16 n. HNO_3, and 400 mg. of PO_4 as H_3PO_4 was heated to fuming, treated with 25 cc. of water and 4 cc. of 3 n. NH_4Cl, placed in a test-tube immersed in boiling water, and treated with H_2S for 10 minutes: a dark precipitate containing 130 mg. of Mo resulted. The mixture was filtered; and the (dark-blue) filtrate was diluted to

100 cc. and saturated cold with H_2S: a brown precipitate containing 100 mg. of Mo resulted. The mixture was filtered, and the (blue) filtrate was evaporated to 15 cc.: a brown precipitate containing 10 mg. of Mo formed. After filtering, the solution (now light-blue) was mixed with 5 cc. of 12 n. HCl, saturated cold with H_2S, and heated 30 minutes in a pressure-bottle in boiling water: a brown precipitate containing 30 mg. of Mo resulted. The mixture was filtered, and the (colorless) filtrate was again saturated with H_2S, and heated as just described: there was only a slight turbidity corresponding to 0.3 mg. of Mo. This experiment shows that, even in the presence of much phosphate, molybdenum is almost completely precipitated when the mixture is treated by the whole of P. 71, but not when the pressure-bottle treatment is omitted.

TELLURIUM GROUP

P. 72, N. 2.—Separation of Selenium from Tellurium by Sulfurous Acid in Concentrated Hydrochloric Acid.—See Keller, *J. Am. Chem. Soc.*, 19, 771 (1897); Noyes and Bray, *ibid.*, 29, 202 (1907).

P. 72, N. 3.—Precipitation of Tellurium by Sulfurous Acid.—In eight separate test-tubes 0.5 mg. of Te as TeO_2 was added to 25 cc. of saturated SO_2 solution and various quantities of 12 n. HCl. The mixtures were heated for 15 minutes in boiling water with the following results:

12 n. HCl added	3 or 4 cc.	5 or 6 cc.	7 cc.	8 cc.	9 or 10 cc.
Precipitate formed	slight	larger	maximum	large	smaller

The maximum effect, obtained with 7 or 8 cc. of 12 n. acid, corresponds to a HCl concentration of 2.6–2.9 n.

100 mg. of Te as TeO_2 were dissolved in 60 cc. of 3 n. HCl and 2 cc. of 95% H_2SO_4, and the mixture was saturated with SO_2 gas and heated 15 minutes on a steam-bath: a dense black precipitate formed. This was filtered out, the filtrate was evaporated to fuming, 40 cc. of 1.5 n. HCl were added, and the mixture was saturated with H_2S: only a white turbidity resulted.

P. 72, N. 4.—Behavior of Lead, Copper, Molybdenum, Iridium, and Rhodium on Heating with Sulfurous Acid.—Various quantities of these elements were in separate experiments dissolved in 30 cc. of 3 n. HCl, and the mixtures were saturated with SO_2 gas and heated in boiling water for 15 minutes, with the following results:

Lead, 50 mg.: no precipitate or color.
Copper, 500 mg.: no precipitate; color becomes deep olive-green.
Molybdenum, 100 mg.: no color.
Iridium, 50 mg.: very dark color changes to very pale olive-green.
Rhodium, 100 mg.: deep-red color, undergoing no change with SO_2.

P. 73. N. 2.—Extraction of Molybdenum with Ether.—As to the preparation of $MoO_3 \cdot 2HCl$, see Pechard, *Compt. rend.*, 114, 173 (1892); Smith and Oberholtzer, *Z. anorg. Chem.*, 4, 236 (1893); Abegg-Auerbach, *Handbuch*, IV, 1, (2), 558 (1921).

As to its extraction by ether, see Pechard, *loc. cit.*; Blair, *J. Am. Chem. Soc.*, 30, 1229 (1908); Swift, *ibid.*, 46, 2378 (1924).

100 mg. of Mo as the c. p. ammonium molybdate of trade after the preliminary treatment shown in the table were dissolved in 5 cc. of 6 n. HCl, and shaken successively with two 15-cc. portions of ether. The amount of molybdenum was determined by precipitating it as sulfide and comparing with standards. The first two experiments were made with different samples of molybdate and with different reagents.

Preliminary treatment of molybdate	*First ether extract*	*Second ether extract*	*Aqueous solution*
None	—	—	6
None	—	—	6
Evaporated with HCl, then with HNO_3	85	12	3
Heated 15 min. with 30 cc. of 3 n. HCl saturated with SO_2, then evaporated	88	2	10

P. 73, N. 3.—Behavior of Bismuth, Cadmium, Copper, Tellurium, Iridium, and Rhodium on Shaking Hydrochloric Acid Solutions with Ether.—Various quantities of these elements were dissolved in 5 cc. of 6 n. HCl, and shaken with the volume of ether indicated below. The total amount extracted by the ether is shown in the next to last column, or in the last column in the cases where the ether extract was washed with 2 cc. of 6 n. HCl before determining its content.

Element	*Milligrams taken*	*Ether used*	*Milligrams in ether extract*	
			before washing	*after washing*
Bi	50	20	0	—
Cd	50	20	2–3	—
Cu	500	15	2	0
Te	50	20	10	—
Ir	50	15	—	0
Rh	100	15	2–3	0

P. 74, N. 1.—Blue Color Test for Molybdenum.—In separate experiments 0.1 mg., 0.5 mg., and 3 mg. of Mo as $(NH_4)_2MoO_4$, dissolved in 5 cc. of 6 n. HCl, were shaken with 15 cc. of ether, and the ether solution was evaporated barely to dryness on a steam-bath in a small casserole: there was no blue color. The residue was dried by moving the dish several times through a gas flame: a deep-blue color developed, which covered more of the dish in the 3-mg. experiment.

300 mg. of Mo as $(NH_4)_2MoO_4$ were evaporated with a mixture of 12 n. HCl and 16 n. HNO_3 to dryness on a steam-bath: the residue was blue, but not very dark. A few drops of 16 n. HNO_3 were added, and the mixture again evaporated to dryness: the residue was now yellow. This was treated with 5 cc. of 6 n. HCl: complete solution did not occur. A few drops of 16 n. HNO_3 were therefore added, and the solution was extracted with 15 cc. of specially purified alcohol-free ether: both layers assumed a deep-yellow color. The ether layer was heated at 50° till most of the ether was expelled: there remained a

small quantity of a yellow sirupy liquid and a light-yellow deposit on the sides of the casserole. The casserole was now placed on a steam-bath: there was a vigorous evolution of gas and a strong odor of aldehyde, and the liquid turned very dark-blue. This experiment shows that ether itself, even when pure, causes the molybdenum to be reduced to the blue compound.

P. 74, N. 3.—Precipitation of Molybdenum by Hydrogen Sulfide after Treatment with Zinc and Thiocyanate.—To 50 mg. of Mo as $(NH_4)_2MoO_4$ were added 2 cc. of 6 n. HCl, 5 cc. of water, 5 cc. of 1 n. KSCN, and 0.1 cc. of granular Zn. After the solution had become deep-red, it was placed in a test-tube immersed in boiling water and treated with H_2S for 10 minutes, and the large brown precipitate filtered off: the (light-green) filtrate contained 3–5 mg. of Mo.

The experiment was repeated, except that the solution was saturated with H_2S cold, instead of at 100°: the filtrate was much darker in color, showing that more molybdenum remained unprecipitated.

P. 75, N. 2.—Behavior of Iridium and Rhodium on Heating the Solution with Nitrous Acid and Making Alkaline.—Various quantities of these elements as chlorides were heated at various temperatures with 10 cc. of water, 5 cc. of 3 n. $NaNO_2$ (or 10 cc. in the experiments where $HCHO_2$ or no acid was added), and the acid shown in the table on the next page. The cold solutions were then treated with NaOH and Na_2CO_3 as indicated. The results are shown in the last column.

The first experiment with iridium and that with rhodium show that 100 mg. of Ir remain completely in solution, and that 100 mg. of Rh give only a slight turbidity, when $HC_2H_3O_2$ is used. The four iridium experiments show that its complete conversion into the complex nitrite occurred when the solution was acidified either with $HC_2H_3O_2$, $HCHO_2$, or HCl, but not when no acid was added. The rhodium experiments show that the conversion is more nearly complete with the weaker acids.

Element	Mgs. taken	Acid added	Heating		Alkali added	Result
			min.	temp.		
Ir	100	1 cc. of 6 n. $HC_2H_3O_2$	5	60–70°	NaOH till alkaline, 1 cc. 3 n. Na_2CO_3.	Clear yellow solution.
	50	0.5 cc. of 6 n. HCl	5	70–80°	NaOH till alkaline.	Clear yellow solution.
	40	None	15	Boiling	None.	Small orange precipitate; yellow solution.
	40	3 cc. of 12 n. $HCHO_2$	1–2	70°	3 n. Na_2CO_3 till alkaline, 2 cc. more, then 1 cc. 6 n. NaOH.	Clear yellow solution.
Rh	100	1 cc. of 6 n. $HC_2H_3O_2$	5	60–70°	NaOH till alkaline, 1 cc. 3 n. Na_2CO_3.	Yellow solution; slight turbidity not coagulated by heating.
	50	0.5 cc. of 6 n. HCl	5	60–70°	20 cc. H_2O, then NaOH till alkaline.	Yellow solution; turbidity coagulated to yellow precipitate on heating.
	20	None	15	Boiling	1 cc. 3 n. Na_2CO_3, 1 cc. 6 n. NaOH.	Pale yellow solution; no precipitate even on heating.
	40	3 cc. of 12 n. $HCHO_2$	1–2	70°	Na_2CO_3 till alkaline, 1 cc. 6 n. NaOH.	No precipitate even on heating.

P. 75, N. 3.—Precipitation of Lead and Copper by Sodium Carbonate.—To 1 mg. of Pb as $Pb(NO_3)_2$ in 15 cc. of 1 n. $NaNO_2$, and 1 cc. of 6 n. $HC_2H_3O_2$, 6 n. NaOH was added till barely alkaline; then 0.5 cc. more and 1 cc. of 3 n. Na_2CO_3 were added: there was no precipitate. Then 1 n. $NaHCO_3$ was added, 1 cc. at a time, waiting 2 or 3 minutes after each addition: a precipitate appeared after 3 cc., and remained after 5 cc., were added.

A solution of 500 mg. of Cu in 15 cc. of 1 n. $NaNO_2$ and 3 cc. of 12 n. HCO_2H was heated to 75°; then 3 n. Na_2CO_3 was added till alkaline, and 2 cc. more; and the large precipitate was filtered out: the filtrate was deep-blue.

To 500 mg. of Cu in 15 cc. of 1 n. $NaNO_2$ 2 cc. of 6 n. $HC_2H_3O_2$ were added, and the mixture was heated 2 minutes at 75°; 6 n. NaOH was added till alkaline, then 3 cc. of 3 n. Na_2CO_3; and the precipitate was filtered out: the filtrate was colorless, and gave no precipitate with H_2S.

P. 75, N. 4.—Separation of Iridium and Rhodium from Copper-Group Elements.—Various quantities of the elements as chlorides were dissolved in 15 cc. of 1 n. $NaNO_2$ and 1 cc. of 6 n. $HC_2H_3O_2$; and the mixture was heated at 60–70° for 5 minutes; 6 n. NaOH was added till litmus was turned blue, then 1 cc. of 3 n. Na_2CO_3; and the mixture was filtered. The results are shown in the table.

Element	*Milligrams taken*	*Milligrams found in*	
		precipitate	*filtrate*
Ir	100	Ir 0	—
Rh	100	Rh 1	—
Cu	500	—	Cu 0
Ir	2	—	Ir 2
Cu	500	—	Cu 0
Rh	1	—	Rh 1
Cu	200	—	Cu 0
Cd	200	—	—
Bi	200	—	—
Pb	1	Pb 1	—
Ir	2	—	Ir >1
Rh	2	—	Rh 2

P. 76, N. 2–4.—Decomposition of the Complex Nitrites of Iridium and Rhodium and their Precipitation with Sodium Hypobromite.—As to the precipitation of iridium by NaBrO from its chloride, see C. E., P. 56, N. 2, 3.

1 mg. of Rh as $RhCl_3$ was heated in a water-bath for 5 minutes with 30 cc. of water and 3 cc. of 3 n. Na_2CO_3: a white precipitate separated. 3 drops of liquid Br_2 were added and the solution warmed: the precipitate was blue at first, but became dark-green after it coagulated.

To 40 cc. of a solution containing 2 mg. of Ir as $Na_3Ir(NO_2)_6$, 15 milliequivalents of $NaNO_2$, 6 milliequivalents of $NaC_2H_3O_2$, and 3 milliequivalents of Na_2CO_3 there were added 25 milliequivalents of HCl (as 6 n. HCl); and the mixture was boiled till the volume decreased to 10 cc.; 3 n. Na_2CO_3 was added till the acid was neutralized, and then 1 cc. more; the solution was heated several minutes in a water-bath, cooled, treated with 2 drops of liquid Br_2, and warmed again; there was a blue-black precipitate corresponding to 2 mg. of Ir.

A solution of 1 mg. of Rh as $Na_3Rh(NO_2)_6$ containing the same substances as in the preceding experiment was boiled down till the volume became 10 cc. To one half of this solution were added 5 cc. of water and 3 n. Na_2CO_3 till the solution became neutral, then 1 cc. more; the solution was heated for 5 minutes in a water-bath: no white precipitate appeared. After cooling, 2 drops of liquid Br_2 were added,

and the mixture again warmed: there was a green color, but no precipitate. The other half of the solution was evaporated with 2–3 cc. of 12 n. HCl till salts crystallized out, and it was then diluted to 10 cc., and treated like the first half: a blue-green precipitate resulted.

To 40 cc. of a solution containing 1 mg. of Rh as $Na_3Rh(NO_2)_6$, 15 milliequivalents of $NaNO_2$, 6 milliequivalents of $NaC_2H_3O_2$, and 3 milliequivalents of Na_2CO_3, 5 cc. of 12 n. HCl were added, and the mixture was evaporated to dryness; the residue was dissolved in 15 cc. of water and 2 cc. of 3 n. Na_2CO_3, and the mixture was heated 5 minutes: there was a white precipitate. The mixture was cooled, treated with 2 drops of liquid Br_2, and heated: a bluish-green precipitate separated. Four more drops of liquid Br_2 were added: the precipitate became lighter green, and some of it apparently dissolved.

The experiment was repeated with 100 mg. of Rh. After adding the Na_2CO_3 and heating, a large yellow precipitate formed. After adding the Br_2 and heating, the precipitate became dark-green. This was filtered off: the filtrate was green. It was heated an hour with occasional addition of a drop of Br_2: a green precipitate coagulated. The mixture was filtered: the filtrate was now colorless.

The experiment was repeated with 50 mg. of Ir as $Na_3Ir(NO_2)_6$. After adding the Na_2CO_3 and heating, a small light-yellow precipitate separated which contained 1 mg. of Ir and some rhodium (due to impurity in the sample). Upon adding the Br_2, a large black precipitate formed. The mixture was heated and filtered: the filtrate was a clear dark-blue. It was heated an hour with occasional addition of Br_2: some precipitate separated. The mixture was filtered: the solution was still dark-blue. 1 cc. of C_2H_5OH was added, and the mixture heated: no precipitate formed. It was shaken with filter-paper pulp and filtered: the pulp was colorless. The solution was saturated with CO_2: no precipitate separated. The solution was evaporated almost to dryness, and the residue treated anew with water, Na_2CO_3, and Br_2 as at the beginning of the experiment: a black precipitate containing 5–8 mg. of Ir separated, and the filtrate was colorless.

70 mg. of Ir as $IrCl_4$ were heated with 20 cc. of water and 2 cc. of 3 n. Na_2CO_3 for 5 minutes on a steam-bath: a large light-colored precipitate separated. The mixture was cooled, and 6 drops of liquid Br_2 were added: a large bluish-black precipitate separated. The mixture was heated for 10 minutes on a steam-bath and filtered; the filtrate was heated 5 minutes longer with 2 drops of liquid Br_2: there was a precipitate containing 15 mg. of Ir. The filtrate from this was heated 10 minutes with 3 drops of liquid Br_2: another precipitate containing about 5 mg. of Ir formed. The filtrate stood a week: 3 mg. of Ir more had separated, and the filtrate was only slightly blue.

P. 77, N. 1.—Dissolving of Iridium and Rhodium Dioxides in Acids. —50 mg. of Ir as IrO_2 (precipitated by NaBrO) were heated for 5 minutes on a steam-bath with 8–10 cc. of 12 n. HCl: there was little action. 0.5 cc. of 16 n. HNO_3 was added, and the heating continued: the precipitate had not entirely dissolved at the end of 30 minutes.

The experiment was repeated using RhO_2 in place of IrO_2: the result was similar.

50 mg. of Rh as precipitated RhO_2 were treated in the cold with 5 cc. of 9 n. HBr: in 5 minutes the RhO_2 entirely dissolved, forming a dark-orange solution.

P. 77, N. 2, 3.—Precipitation of Iridium by Ammonium Chloride.— In five experiments 0.1 mg. of Ir as $IrCl_4$ was dissolved in 1 cc. of water, and the solution was saturated with NH_4Cl and treated as follows, with the results indicated:

a, let stand 12 hours: bluish-black flocculent precipitate (of IrO_2).
b, 0.04 cc. of 12 n. HCl added, let stand 12 hours: no precipitate.
c, 0.04 cc. of 12 n. HCl added, saturated with Cl_2, let stand 12 hours: black precipitate.
d, 0.04 cc. of 12 n. HCl added, saturated with Cl_2, heated, let stand 12 hours: small black precipitate.
e, saturated with Cl_2, let stand 20 minutes, heated on steam-bath, cooled: black precipitate.

In three experiments 0.3 mg. of Ir as $IrCl_4$ was dissolved in 1 cc. of 0.5 n. HCl. In the first one, the solution was saturated cold with NH_4Cl and Cl_2, and then let stand. In the second one it was so saturated, let stand 15 minutes, heated 15 minutes on a steam-bath, and cooled. In the third one, the solution was first saturated cold with Cl_2, heated to 50° for 2–3 minutes, cooled, saturated with NH_4Cl, heated 15 minutes on a steam-bath, and cooled. In the first case a precipitate formed only after 2 hours; in the second case it formed immediately; and in the third case, also immediately, but in larger quantity.

A solution of 0.5 mg. of Ir as H_2IrCl_6 in 1 cc. of water was acidified with 2 drops of HCl and saturated with NH_4Cl: within half an hour a black precipitate had separated.

A solution of 50 mg. of Ir as $IrCl_4$ in 2 cc. of water was saturated with Cl_2, heated 3 minutes at 50°, saturated with NH_4Cl, heated 15 minutes on a steam-bath, cooled, and allowed to stand 15 minutes: a black precipitate containing about 40 mg. of Ir formed. The solution was decanted and saturated with Cl_2: a small precipitate formed. The mixture stood several hours: there was little increase in the precipitate. The mixture was heated 15 minutes on the steam-bath, cooled, and

let stand 10 minutes: there was now a precipitate corresponding to 5–6 mg. of Ir; and the filtrate was still dark-yellow. The iridium in it was estimated by further treatment to be 2–3 mg.

P. 77, N. 3.—Non-Precipitation of Rhodium by Ammonium Chloride.—A solution of 100 mg. of Rh as $RhCl_3$ in 2 cc. of water was saturated with Cl_2, heated, cooled, saturated with NH_4Cl, heated again, cooled, and allowed to stand several hours: no precipitate separated.

P. 78, N. 1.—Precipitation of Rhodium as Chloro-pentammino-rhodium Chloride.—1 mg. of Rh as $RhCl_3$ in 2 cc. of saturated NH_4Cl and 3 cc. of 15 n. NH_4OH was evaporated to dryness, the residue dissolved in 2 cc. of hot 6 n. HCl, the mixture cooled, and let stand 15 minutes: a slightly yellow, crystalline powder separated.

The experiment was repeated with 0.5 mg. of Rh: there was a slight precipitate.

The experiment was repeated (with 1 mg. of Rh), except that the mixture was heated in a pressure-bottle 30 minutes before being evaporated: the result was the same.

The experiment was twice repeated with the change that the NH_4Cl solution was first evaporated to dryness and then heated 30 minutes in a pressure-bottle with 3 cc. of 15 n. NH_4OH; in one case the residue after evaporation was heated with 2 cc. of 6 n. HCl, in the other with 2 cc. of 6 n. NH_4OH: in both cases a slightly yellow powder remained.

A solution of 100 mg. of Rh as $RhCl_3$ in 2 cc. of saturated NH_4Cl and 3 cc. of 15 n. NH_4OH was evaporated to dryness, and the residue was heated with 2 cc. of 6 n. HCl: a large bright-yellow precipitate remained. The mixture was cooled and allowed to stand: the solution above the precipitate was deep-yellow. The solution was evaporated repeatedly with HCl and HNO_3 (to destroy ammonium salts), the residue was dissolved in 10 cc. of dilute HCl, and saturated hot with H_2S: a black precipitate corresponding to 1 mg. of Rh separated.

Non-Precipitation of Iridium by Digestion with Ammonium Hydroxide and Addition of Hydrochloric Acid.—5 mg. of Ir as $IrCl_3$ were heated in a pressure-bottle in boiling water with 1 cc. of saturated NH_4Cl and 3 cc. of 15 n. NH_4OH for 30 minutes; the solution was evaporated to a few drops, heated to boiling with 2 cc. of 6 n. HCl, filtered, and cooled: no precipitate separated.—The experiment was repeated, using $IrCl_4$ instead of $IrCl_3$, and omitting the heating under pressure: the result was the same.

COPPER GROUP

P. 81–85.—Analysis of the Copper Group.—See Noyes and Bray, *J. Am. Chem. Soc.*, 29, 196–199 (1907).

PRECIPITATION AND PARTIAL ISOLATION OF THE ALUMINUM, NICKEL, ZIRCONIUM, AND RARE-EARTH GROUPS

GENERAL DISCUSSION

D. 92.—Behavior of Gallium and Vanadium with Ammonium Hydroxide and Sulfide.—See C. E., P. 92, N. 5.

D. 92.—Precipitation of Phosphates of the Alkaline-Earth Elements by Ammonium Hydroxide.—See N–B–S, 534, for the results of experiments with small amounts of phosphate.*

To determine how completely magnesium is precipitated by NH_4OH when much phosphate is present, a solution containing in 100 cc. 10 mg. of Mg as $Mg(NO_3)_2$, 30 milliequivalents of $HClO_4$, and 500 mg. of PO_4 as H_3PO_4 was neutralized with 6 n. NH_4OH, and an excess of not more than 1 cc. was added: there was a small white precipitate. The mixture was heated to boiling, cooled and allowed to stand for 3 hours: there was a small crystalline precipitate corresponding to not more than 2 mg. of Mg.—The experiment was repeated, except that 3 cc. of 6 n. NH_4OH were added in excess, and the mixture was not heated to boiling: a much larger precipitate formed than before, and the filtrate was found to contain only 0.5 mg. of Mg, showing that when much phosphate is present magnesium may be almost completely precipitated at this point.

D. 96.—Co-Precipitation by Ammonium Hydroxide of Cobalt, Nickel, or Zinc with the Hydroxides of Chromium, Titanium, Zirconium, Thorium, Iron, or Aluminum.—As to the carrying down of zinc with chromium hydroxide see N–B–S, 526.

In each of the experiments tabulated below 2 mg. or 20 mg. of Co, Ni, or Zn as nitrate were mixed with 100 or 200 mg. of the element listed in the first column, 5 cc. of 6 n. HCl were added, and the mixture was diluted to 100 cc. To the cold solution was added 15 n. NH_4OH, 0.5 cc. at a time, with stirring, to alkaline reaction, and then an excess of 2–2.5 cc. (In the experiments with 200 mg. of Al only 2.5 cc. of 6 n. NH_4OH, instead of 15 n., were added in excess.) The mixture was heated to boiling, cooled, and filtered. Both the filtrate and the precipitate (except when the results are within parentheses) were analyzed for cobalt, nickel, or zinc.

The filtrates were analyzed by passing H_2S into the ammoniacal

* In the following pages the abbreviation N–B–S followed by a number refers to a page in the article by Noyes, Bray, and Spear, *J. Am. Chem. Soc.*, 30, 481–563 (1908), entitled A System of Qualitative Analysis for the Common Elements. Part III: Analysis of the Aluminum and Iron Groups, including Beryllium (Glucinum), Uranium, Vanadium, Titanium, Zirconium, and Thallium.

solution, and estimating the quantity of cobalt, nickel, or zinc from the size of the precipitate of CoS, NiS, or ZnS. The precipitates containing zirconium, thorium, or aluminum were analyzed by dissolving them in HCl, adding $NH_4C_2H_3O_2$; and from the resulting acid-acetate solution precipitating the zinc as ZnS by H_2S (see D. 97 and P. 123), the nickel as nickel dimethylglyoxime and the cobalt as $K_3Co(NO_2)_6$. The precipitates containing ferric iron were dissolved in 7 n. HCl, and extracted with ether as in P. 93, the aqueous layers were evaporated to dryness, and the zinc, nickel, or cobalt precipitated in acetic acid solution as ZnS, as nickel dimethylglyoxime, or as $K_3Co(NO_2)_6$. The results are as follows.

	2 mg. of Co, Ni, or Zn added		*20 mg. of Co, Ni, or Zn added*	
	Filtrate	*Precipitate*	*Filtrate*	*Precipitate*
100 Ti as $TiO(SO_4)$	0.05 Co	(1.95 Co)	1.5 Co	(18.5 Co)
	0.4 Ni	(1.6 Ni)	5 Ni	(15 Ni)
	0.4 Zn	(1.6 Zn)	5 Zn	(15 Zn)
100 Zr as $ZrO(NO_3)_2$.....	0.1 Co	(1.9 Co)	2 Co	(18 Co)
	0.7 Ni	1.3 Ni	10 Ni	10 Ni
	0.6 Zn	(1.4 Zn)	10 Zn	10 Zn
100 Th as $ThO(NO_3)_2$ ...	1 Co	1 Co	6 Co	14 Co
	1.2 Ni	0.8 Ni	15 Ni	5 Ni
	1.5 Zn	0.5 Zn	15 Zn	5 Zn
200 Al as $Al(NO_3)_3$.....	0.0 Co	2.0 Co	1.0 Co	19 Co
	0.01 Ni	1.99 Ni	5 Ni	15 Ni
	0.05 Zn	1.95 Zn	0.5 Zn	19.5 Zn
200 Fe as $Fe(NO_3)_3$.....	0.01 Co	1.99 Co	0.5 Co	19.5 Co
	0.4 Ni	1.6 Ni	16 Ni	4 Ni
	0.5 Zn	1.5 Zn	5 Zn	15 Zn

100 mg. of Th and 50 mg. of Co as nitrates were dissolved in 35 cc. of water containing 5 cc. of 6 n. HNO_3. This solution was poured all at once into 35 cc. of NH_4OH containing 75 milliequivalents, at a temperature of about 25°. The large pink precipitate was filtered off at once, washed, dissolved in HCl, and treated with H_2S in the presence of $NH_4C_2H_3O_2$ and a little $HC_2H_3O_2$: about 10 mg. of Co were found to have precipitated with the thorium. The remaining 40 mg. of Co were found in the filtrate.

In each of the 5 following experiments, a mixture of 200 mg. of Ti as $TiOSO_4$, 50 mg. of Co as $Co(NO_3)_2$, and 30 milliequivalents of HNO_3 was treated with 75 milliequivalents of NH_4OH, using the two liquids at such concentrations as to make the total volume about 70 cc. The precipitate was blue at the end of each experiment. The filtrate contained no titanium, and the amount of cobalt in it was estimated from the size of the CoS precipitate obtained with H_2S.

(a) The acid solution (35 cc.) was poured, a small portion at a time, into 35 cc. of NH_4OH at 25°, the mixture being stirred after each addition: the filtrate contained 5 mg. of Co (and the precipitate 45 mg. of Co).

(b) The same, except that the acid solution was added as rapidly as possible: the filtrate contained 8 mg. of Co.

(c) NH_4OH was poured intermittently, with stirring, into 50 cc. of acid solution at 25°: the filtrate contained 5 mg. of Co.

(d) The same as (c), except that the temperature was about 60°: the filtrate contained 5 mg. of Co.

(e) The same as (c), except that the acid solution also contained 1 g. of NH_4NO_3: the filtrate contained 12 mg. of Co.

In spite of the variation in the methods of mixing the solutions, 38–45 mg. of Co (out of 50 mg.) were always carried down with 200 mg. of Ti precipitated as hydroxide by NH_4OH. However, there is definite evidence in (e) that the separation is improved by increasing the concentration of ammonium salt.

In another series, a mixture of 20 mg. of Zn and 50 mg. of a second element as chlorides or nitrates was treated with NH_4OH, the mixture was heated to boiling, allowed to cool, and filtered. An excess of 2 cc. of 6 n. NH_4OH was used, the final volume was about 28 cc., and 18–24 milliequivalents of NH_4Cl were present. The quantity of zinc in each filtrate was determined by the $K_4Fe(CN)_6$ titration method of Waring, *J. Am. Chem. Soc.*, **26**, 4 (1904), and that in the precipitate calculated by difference. The proportion of the zinc in the precipitates is shown in the table.

20 mg. of	Zn	Zn	Zn	Zn	Zn
50 mg. of	Ti	Al	Zr	Fe	Be
% Zn in ppt.	53	48	23	21	8

Adsorption of Cobalt by Titanium Hydroxide or Ferric Hydroxide. —100 mg. of Ti were precipitated as $TiO(OH)_2$ by NH_4OH in the cold from 100 cc. of an acid solution containing chloride and sulfate, 3 cc. of 15 n. NH_4OH being added in excess; the mixture was boiled for 2 minutes and allowed to cool. To it were added 10 cc. of a solution containing 2 mg. of Co as nitrate and a small excess of NH_4OH: in the cold the $TiO(OH)_2$ precipitate acquired a faint-blue tint. The mixture was then boiled gently for 5 minutes: the precipitate rapidly became distinctly blue and the solution colorless. The filtrate was tested with H_2S, and estimated to contain only 0.04 mg.–0.05 mg. of Co.

The experiment was repeated, except that before the excess of NH_4OH was added the titanium was almost completely precipitated in acid solution by boiling the mixture after each addition of NH_4OH to

the acid solution: after the addition of the cobalt in the cold, the precipitate remained white for 15 minutes; but when the mixture was boiled the precipitate became light-blue and the solution colorless. The filtrate contained not more than 0.07 mg. of Co.

The first experiment was repeated twice with 2 mg. and once with 20 mg. of Co, except that 100 mg. of Fe as $Fe(OH)_3$ were used instead of the titanium: with 2 mg. of Co, after 5 minutes in the cold, the filtrate contained 0.5 mg. of Co; with 2 mg. of Co, after the boiling, it contained only 0.03 mg. of Co; while with 20 mg. of Co, after the boiling, it contained only 1 mg. of Co.

These experiments demonstrate the great adsorptive capacity of the highly-dispersed flocculent precipitates of titanium and ferric hydroxides for cobalt in the presence of ammonium hydroxide.

Adsorption of Zinc by Aluminum Hydroxide.—200 mg. of Al were precipitated as $Al(OH)_3$ in the cold from 100 cc. of a solution containing chloride, nitrate, and 30 milliequivalents of acid, 3 cc. of 6 n. NH_4OH being added in excess; the mixture was boiled gently for 2 minutes, and cooled. To it were added 10 cc. of a solution containing 2 mg. of Zn as nitrate dissolved in a small excess of NH_3OH, the mixture was boiled for 2 minutes, cooled, and filtered: the filtrate with H_2S gave a precipitate corresponding to 0.2 mg. of Zn, and the remainder of the zinc was shown to be in the precipitate.—The experiment was repeated with 20 mg. of Zn: the filtrate contained only 3 mg. of Zn, and the remaining 17 mg. were taken up by the $Al(OH)_3$.

After the articles by Ardagh with Broughall and Bongard were published (see below), a number of additional experiments were made with zinc and aluminum. It was found that for a sample of aluminum hydroxide prepared under definite conditions the equilibrium distribution of zinc between the precipitate and solution was approximately the same, whether the zinc was precipitated with the aluminum or afterwards adsorbed from the solution. The rate of adsorption was very great at high temperature, and rather slow at room temperature. The proportion of the zinc in the solution increased as the concentration of either ammonium salt or ammonium hydroxide at the time of precipitation is increased; and these two effects are approximately additive when the concentrations of these two substances are simultaneously increased. The zinc is not appreciably extracted from the precipitate by water; the proportion of it removed by a solution containing ammonium hydroxide and an ammonium salt increases with the concentration of each of these substances.

Separation of Nickel, of Zinc, and of Cobalt from Ferric Iron and Aluminum by Ammonium Hydroxide and Chloride.—Ardagh and

Broughall, *Can. Chem. Met.*, 7, 198 (1923), and Ardagh and Bongard, *J. Ind. Eng. Chem.*, 16, 297 (1924), show that a complete separation of nickel and zinc from ferric iron is attained by the following process. To a solution in 2–3 cc. of warm dilute HCl 5 g. of powdered NH_4Cl are added, the mass is well stirred, 10 cc. of 16 n. NH_4OH are added, and the mixture is thoroughly agitated, diluted with 25 cc. of cold water, and filtered. In the second article it is shown that this method also prevents zinc from being retained by $Al(OH)_3$, but that a small amount of aluminum is dissolved.

The results of new experiments made by the process just described are given below. In the cases where only 2 mg. of Ni or Co were taken, the quantities of these elements in the filtrate were determined by comparing the H_2S precipitates with standards. In the other cases the NH_4OH precipitates were dissolved in 6 n. HCl, the $FeCl_3$ was extracted with ether (P. 93), the aqueous layer was evaporated and tested for nickel or zinc with NH_4OH and H_2S, or for cobalt with KNO_2 and $HC_2H_3O_2$.

Milligrams taken	*Milligrams found in filtrate*	*precipitate*
100 Fe, 2 Ni	1.5–2.0 Ni	—
100 Fe, 2 Co	1.5–2.0 Co	—
100 Fe, 50 Ni	—	<0.1 Ni
100 Fe, 50 Zn	—	<0.1 Zn
100 Fe, 50 Co	—	1.0 Co

D. 97.—Precipitation of Elements from Acid Acetate Solutions by Hydrogen Sulfide.—A solution containing in a total volume of 110 cc. 15 milliequivalents each of NH_4Cl and NH_4ClO_4, one milligram of the element shown in the first column (in the form of nitrate), the number of milliequivalents of $HC_2H_3O_2$ and of $NH_4C_2H_3O_2$ shown in the second and third columns, was saturated with H_2S in the manner shown in the fourth column with the results shown in the last column.

Element taken	Milliequivalents of		Way of saturating with H_2S	Result
	$HC_2H_3O_2$	$NH_4C_2H_3O_2$		
1 Co	39	39	15 min., hot. Stood 60 min.	No ppt. No ppt.
1 Ni	39	39	2 min., hot. 5 min., hot.	Turbidity. Black ppt.
1 Ni	6	39	1 min., hot. 3 min., hot.	Turbidity. Black ppt.
1 Co	22	22	10 min., cold. Heated to 80–90°.	No ppt. Black ppt.
1 Ni	22	22	10 min., cold. Heated to 80–90°.	No ppt. Black ppt.
1 Co	39	39	10 min., cold. Heated to 80–90°.	No ppt. Black ppt., slowly.
2 In[a]	6	39	30 sec., cold. Heated to 70–80°, stood 5 min.	Yellow turbidity. Yellow ppt.
1 In[a]	6	39	10 min., hot. Stood 30 min.	Yellow turbidity. Yellow ppt.
1 In[a]	30	30	Saturated in cold. Heated to 70°, cooled, saturated. Stood 30 min.	Yellow color; no ppt. Yellow turbidity. Yellow flocks.
1 Fe[b]	6	39	1 min., cold. 10 min., cold. Heated to 80–90°.	Black turbidity. Small black ppt. Black ppt.
1 Fe	22	22	20 min., cold. Heated to 80–90°.	No ppt. No ppt.
1 Zn	6	39	2 min., hot. Stood 90 min.	Turbidity. Flocculent ppt.
1 Zn	39	39	2 min., cold. Heated to 80–90°, stood 1 hr.	Turbidity. Flocculent ppt.
1 Zn	22	22	Same as preceding.	Same as preceding.

[a] As $InCl_3$.

[b] After boiling 1–2 min. the precipitate dissolved, but it reappeared when H_2S was passed into the solution and it had cooled to about 60°.

Solutions containing in a total volume of 110 cc. the number of milligrams of the elements (always in the form of nitrate) shown in the first column of the following table, together with 39 milliequivalents of $NH_4C_2H_3O_2$, 6 milliequivalents of $HC_2H_3O_2$, and 15 milliequivalents each of NH_4Cl and NH_4ClO_4, were saturated with H_2S. The mixtures were then filtered, and the precipitates and filtrates were analyzed by the methods indicated in the last two columns; the final precipitates being always compared with those given by known quantities of the elements: the results are given in the second and third columns.

In the experiments shown in the part of the table below the dotted line a somewhat more effective treatment with H_2S was used, which consisted in heating the solution almost to boiling, passing H_2S slowly as long as it was absorbed, cooling the mixture, saturating it again, and then heating it almost to boiling.

Quantity taken	*Found in precipitate*	*Found in filtrate*	*Precipitate tested by*	*Filtrate tested by*
500 Zn	——	0 Zn	——	NH_4OH and H_2S.
500 Zn	——	——	——	——
2 Mn	——	1 Mn	——	$(NH_4)_2S$, then Na_2O_2.
400 Zn	Large Zn	——	Appearance.	——
30 U	0.5 U	Large U	NH_4OH and NH_4Cl.	NH_4OH and H_2S.
500 Zn	——	——	——	——
2 U	——	1.2 U	——	$(NH_4)_2S$, then K_4FeCy_6
250 Zn[a]	Large Zn	1–2 Zn	Appearance.	$(NH_4)_2S$; $HC_2H_3O_2$, H_2S
450 Mn	10 Mn	Large Mn	NaOH and Na_2O_2.	$(NH_4)_2S$.
500 Zn	Large Zn[b]	——	Appearance.	——
2 Cr	1.3 Cr	0.7 Cr	NaOH and Na_2O_2.	NH_4OH, then Na_2O_2.
250 Co	Large Co	1–2 Co	Appearance.	NH_4OH and H_2S.
250 Ni	Large Ni	1–2 Ni	Appearance.	NH_4OH and H_2S.
2 Mn	0 Mn	1 Mn	HNO_3 and $KClO_3$.	NH_4OH, H_2S; then HNO_3 and $KClO_3$.
500 Zn	Large Zn[c]	0 Zn	Appearance.	$(NH_4)_2S$.
1 Fe	1 Fe	0 Fe	NH_4OH and HN_4Cl.	$(NH_4)_2S$.
500 Co	Large Co	1.5 Co[d]	Appearance.	$NH_4C_2H_3O_2$ and H_2S.
1 Be	——	1 Be	——	NH_4OH after expelling H_2S.
500 Zn	Large Zn	0 Zn	Appearance.	——
1 Be	——	1 Be	——	NH_4OH after expelling H_2S.
250 Co	Large Co	0 Co	Appearance.	$(NH_4)_2S$.
250 Ni	Large Ni	0 Ni	Appearance.	$(NH_4)_2S$.
2 Cr	1 Cr	0 Cr	NaOH and Na_2O_2.	NH_4OH, then Na_2O_2.
500 Mn	0 Mn	Large Mn	Appearance.	——
10 U	10 U	0 U	$(NH_4)_2S$.	$(NH_4)_2S$, then K_4FeCy_6
10 U[e]	0.8 U	9 U	$K_4Fe(CN)_6$.	NH_4OH.
400 U	Large U	0.5 U	Appearance.	NH_4OH and H_2S.

[a] This mixture contained 45 milliequivalents (instead of 39) of $NH_4C_2H_8O_2$ and 6 milliequivalents of $HC_2H_3O_2$.

[b] Large bluish-white precipitate.

[c] Large dark-red colored precipitate.

[d] This was all precipitated by adding 5 cc. of 3 n. $NH_4C_2H_3O_2$ and heating.

[e] This solution contained 22 milliequivalents each of $HC_2H_3O_2$ and $NH_4C_2H_3O_2$ instead of 6 and 39 milliequivalents respectively.

THE ACETATE PRECIPITATE: PROCEDURES AND NOTES

EXPERIMENTS ON P. 92–94 BY ERNEST H. SWIFT

P. 91, N. 2, 3.—Extraction of Ferric Chloride, Gallium Chloride, and Thallic Chloride by Ether from Hydrochloric Acid Solution.—See C. E., P. 93, N. 2, 3.

P. 92, N. 1.—Oxidation of Quadrivalent Vanadium by Bromine in Dilute Acid Solution.—See N–B–S, 551.

P. 92, N. 2–8.—Precipitation of Iron by Boiling with Ammonium Acetate and Acetic Acid, and the Effect of Certain Other Elements.—In the experiments tabulated below, to the amount of iron as $Fe(NO_3)_3$, or of iron with another element, indicated in the second column and contained in 100 cc. of solution, were added 6 n. HCl and 3 n. $NH_4C_2H_3O_2$ reagent until the quantities present of $HC_2H_3O_2$, $NH_4C_2H_3O_2$, and NH_4Cl (before reaction with iron or other element) were those given in the third, fourth, and fifth columns. The solution was then boiled gently in a covered flask for the time shown in the sixth column and filtered. The amounts of iron (and other elements) in the precipitate and filtrate are indicated in the seventh and eighth columns. (For the table see the next page.)

From these experiments the following conclusions may be drawn. Iron cannot be precipitated completely from a boiling solution when the ratio of $HC_2H_3O_2$ to $NH_4C_2H_3O_2$ is very high (Expt. 7). The highest possible ratio under the conditions of these experiments is about 42/3, and in this case long boiling is necessary (Expts. 6, 5).

The presence of ammonium salts favors the precipitation (Expts. 9, 10, 6), presumably by coagulating the colloid.

For the precipitation of aluminum a lower ratio of $HC_2H_3O_2$ to $NH_4C_2H_3O_2$ is required than for iron alone (Expts. 13, 12, 4).

The presence with the iron of cerium or thorium (but not scandium) has a marked effect in forming stable colloidal solutions (Expts. 19, 20, 18), but precipitation is complete when phosphate is added (Expt. 21).

Expt.	Milligrams	Milliequivalents of			Minutes boiled	Milligrams found in		Remarks
		HAc	NH_4Ac	NH_4Cl		*precipitate*	*filtrate*	
1	1 Fe	6	39	6	2	1 Fe	0	
2	10	18	27	18	2	10	0	
3	10	30	15	30	2	10	0	
4	10	36	9	36	2	10	0	
5	10	42	3	42	2	2–3	7–8	Ppt. didn't coagulate.
6	10	42	3	42	4	10	0	
7	10	48	0	48	5	1–2	8–9	
8	10	45[a]	0	45	3	No ppt.	10	
9	10	42	3	0	3	No ppt.	10	
10	10	42	3	30	3	2–3	7–8	
11	10	42	6	30	3	10	0	
12	10 Fe 10 Al	24	21	24	5	No ppt.	10 Fe 10 Al	
13	10 Fe 10 Al	18	27	18	2	Ppt.	Trace Fe 3–5 Al	
14	300 Fe	6	39	6	2	300 Fe	0 Fe	
15	300 Fe	18	27	18	2	300 Fe	0 Fe	
16	300 Fe	24	21	24	2	Large ppt.	1–2 Fe	
17	300 Fe	30	15	30	2	" "	Colloidal 15–20 Fe	
18	200 Fe 100 Sc	6	39	30	2	Large ppt.	0 Fe 10–15 Sc	
19	200 Fe 100 Th	6	39	30	2	Colloidal		Coagulated when solution was neutralized.
20	200 Fe 100 Ce	6	39	30	2	No ppt.	200 Fe 100 Ce	Ppt. when solution was neutralized.
21	200 Fe 100 Ce 230 PO_4[b]	6	39	30	2	Large ppt.	0 Fe 0 Ce	

[a] Also 3 milliequivalents of HCl. [b] As Na_2HPO_4.

P. 92, N. 3–8.—Behavior of Various Elements on Boiling with Ammonium Acetate and Acetic Acid.—In each of the experiments in the following tables to 100 cc. of a solution containing the listed quantities of the various elements and containing (unless otherwise stated) 30 milliequivalents of HCl there were added NH_4OH and $NH_4C_2H_3O_2$ reagent in such quantities as to produce the milliequivalents of $HC_2H_3O_2$ and $NH_4C_2H_3O_2$ (before the reaction with iron or other element took place) that are shown in the third and fourth columns. The mixture (having a volume of about 120 cc.) was boiled gently in a covered flask for the time indicated and was filtered, and the content of the precipitate and filtrate determined by analysis, with the results shown. The precipitation of iron was complete, unless otherwise stated.

Element	Substance	Milliequivalents		Minutes boiled	Precipitate	Filtrate	Footnote
		$HC_2H_3O_2$	NH_4-$C_2H_3O_2$				
1 Al	$Al(NO_3)_3$	6	39	2	Turbidity	——	*a*
2 Al	"	6	39	2	Small	0 Al	*a*
10 Al	"	6	39	2	Medium	1 Al	*a*
300 Al	"	6	39	2	15–30 Al	——	*a, b*
1 Ti	$TiOSO_4$	6	39	2	Small	——	*a*
10 Ti	"	6	39	2	Medium	0 Ti	*a*
1 Zr	$Zr(NO_3)_4$	6	39	2	Small	——	*a*
50 Zr	"	6	39	2	Large	½ Zr	*a*
10 W	$(NH_4)_2WO_4$	12	33	7	None	10 W	
20 W	"	24	21	2	None	20 W	
10 W 150 Fe	$(NH_4)_2WO_4$ $Fe(NO_3)_3$	12	11½	2	Large	½ W ½ Fe	*c*
5 W 300 Fe 50 PO_4	$(NH_4)_2WO_4$ $Fe(NO_3)_3$ Na_2HPO_4	14	31	5	Large	1 W 0 Fe 0 PO_4	
25 W 300 Fe 50 PO_4	"	14	31	5	Large	0.5–1 W 0 PO_4	
50 V	NH_4VO_3	6	39	5	None	50 V	*d*
1 V 300 Fe	NH_4VO_3 $Fe(NO_3)_3$	6	39	2	Large	0 V	*d*
10 V 300 Fe	"	14	31	5	Large	0 V	
50 V 300 Fe	"	6	39	2	Large	0 V	
300 Cr	$Cr(NO_3)_3$	12	33	5	2–3 Cr	——	
2 Cr 200 Fe	$Cr(NO_3)_3$ $Fe(NO_3)_3$	6	39	2	Large 2 Cr	0 Cr	
300 Cr 300 Fe	"	12	33	2	Large	15–20 Cr 3–5 Fe	
5 In	$InCl_3$	6	39	2	None	5 In	
5 In	"	3	42	2	None	5 In	
2 In 300 Fe	$InCl_3$ $Fe(NO_3)_3$	6	39	2	Large 1.5 In	½ In	
20 In 300 Fe	"	6	39	2	Large 19–20 In	½ In	
500 Zn	$Zn(NO_3)_2$	6	39	5	None	500 Zn	
300 Zn 300 Fe	$Zn(NO_3)_2$ $Fe(NO_3)_3$	6	39	2	Large 15–25 Zn	——	
20 Zn 300 Cr 300 Fe	$Zn(NO_3)_2$ $Cr(NO_3)_3$ $Fe(NO_3)_3$	6	39	2	Large 10 Zn	10 Zn 2–3 Cr ½ Fe	*e*

[a] The solution contained only 6 milliequivalents of NH_4Cl, not 30.

[b] A colloidal solution resulted, and the 15–30 mg. of Al as $Al(OH)_3$ was collected on a filter only after the mixture had stood several hours.

[c] The volume of the solution in this experiment was 50 cc.

Element	Substance	Milliequivalents		Minutes boiled	Precipitate	Filtrate	Footnote
		$HC_2H_3O_2$	NH_4-$C_2H_3O_2$				
2 Zn 200 Cr 300 Fe	$Zn(NO_3)_2$ $Cr(NO_3)_3$ $Fe(NO_3)_3$	6	39	2	Large	1–2 Zn	*e*
2 Zn 100 Zr 100 Ti 300 Fe	$Zn(NO_3)_2$ $Zr(NO_3)_4$ $TiOSO_4$ $Fe(NO_3)_3$	6	39	2	Large	1½–2 Zn	*e*
200 Mn	$Mn(NO_3)_2$	14	31	5	None	200 Mn	
200 Mn 300 Fe	$Mn(NO_3)_2$ $Fe(NO_3)_3$	14	31	2	Large <1 Mn	——	
0.7 Mn 300 Fe	"	6	39	2	Large	0.05 Mn	
1 Mn 300 Fe	"	6	39	2	Large	0.6 Mn	
2 Mn 300 Fe	"	6	39	2	Large	1 Mn	
2½ Mn 200 Fe 380PO_4	$Mn(NO_3)_2$ $Fe(NO_3)_3$ Na_2HPO_4	6	39	2	Large	2–2½ Mn	
100 Ce 100Mn 200 Fe 475PO_4	$Ce(NO_3)_3$ $Mn(NO_3)_2$ $Fe(NO_3)_3$ Na_2HPO_4	6	39	2	Large 5–10 Mn	——	
1 Ni 300 Fe	$Ni(NO_3)_2$ $Fe(NO_3)_3$	6	39	2	Large	½ Ni	
200 Ni 300 Fe	"	6	39	2	Large 20 Ni	——	
1 Co 300 Fe	$Co(NO_3)_2$ $Fe(NO_3)_3$	6	39	2	Large	0.8–1.0 Co	
200 Co 300 Fe	"	6	39	2	Large 20 Co	——	
100 Be	$BeSO_4$	12	33	3	5–10 Be	——	
100 Be	"	0	45	2	40–50 Be	——	*f*
25 Be 300 Fe	$BeSO_4$ $Fe(NO_3)_3$	12	33	2	Large 2–3 Be	1 Fe	
50 Th	$Th(NO_3)_4$	6	39	7	5–10 Th	——	
50 Sc	$ScCl_3$	6	39	5	None	50 Sc	
100 U	$UO_2(NO_3)_2$	6	39	7	None	100 U	
50 U 300 Fe	$UO_2(NO_3)_2$ $Fe(NO_3)_3$	6	39	2	Large 3–6 U	——	

d The acid solution of the vanadium was saturated with H_2S, the H_2S then expelled by boiling, and then a slight excess of Br_2 added before adding the NH_4OH and $NH_4C_2H_3O_2$.

e After the treatment indicated in the table, 12 cc. of 6 n. NH_4OH were added and the mixture was boiled two minutes longer. The results shown in the table are those observed after this second treatment.

f The final solution was faintly acid to litmus. 2 cc. of 6 n. NH_4OH completed the precipitation and made the solution distinctly alkaline.

Two experiments in the preceding tables with 1 and 50 mg. of zirconium show that its precipitation is practically complete when the initial ratio of acetic acid to acetate is as low as 6/39. On the other hand, N–B–S, 557–8, found 1–5 mg. of Zr in the filtrate from the acetate treatment, with zirconium alone and with iron. The discrepancy is doubtless due to a higher ratio of acetic acid to acetate in the N–B–S experiments. As to the fact that when this ratio is high zirconium is not precipitated, and that it then prevents the complete precipitation of titanium, see Hillebrand, *Bull. U. S. Geol. Survey,* **422,** 136 (1916); **700,** 163 (1919).

As to the incomplete precipitation of aluminum in the acetate treatment when the acetic acid concentration is high, see C. E., P. 92, N. 2–8, Expts. 12 and 13; also Hillebrand, *Bull. U. S. Geol. Survey,* **422,** 100 (1916); **700,** 110 (1919).

As to the fact that certain of the rare-earth elements may pass completely into the filtrate, see Hillebrand, *Bull. U. S. Geol. Survey,* **422,** 100 (1916); **700,** 109 (1919). See also the experiments with scandium and thorium alone in the preceding table.

P. 92, N. 5.—Precipitation of Gallium on Boiling with Ammonium Acetate and Acetic Acid.—In the experiments recorded in the following table, to various amounts of Ga as $Ga(NO_3)_3$ present in 100 cc. of solution were added 6 n. HCl (or 6 n. $HClO_4$ where a star is inserted) and then 6 n. NH_4OH and 3 n. $NH_4C_2H_3O_2$ (made neutral to litmus), or $NH_4C_2H_3O_2$ alone, until the quantities initially present of $HC_2H_3O_2$, $NH_4C_2H_3O_2$, and NH_4Cl (or NH_4ClO_4) were those given in the table. The solution was then boiled gently in a covered 300-cc. conical flask for the time indicated, and examined for a precipitate. In the experiments where an *a* is affixed in the last column the filtrate was tested for gallium by diluting it to 150 cc. and boiling it 5 minutes.

Experiments 1–3 seem to show that a large concentration of $NH_4C_2H_3O_2$ is not favorable to the precipitation of small amounts of gallium, although larger amounts of gallium are precipitated practically completely. Even with a concentration of $NH_4C_2H_3O_2$ as large as 39 milliequivalents in 100 cc., 2.5 mg. of gallium give a precipitate on boiling 5 minutes (Expt. 3). The best conditions for the precipitation of small quantities of gallium seem to require about 6 milliequivalents of $HC_2H_3O_2$ and 9 of $NH_4C_2H_3O_2$ in a volume of 100 cc. The presence of perchlorate or chloride in the solution has no effect (Expts. 15–16). Experiments 17 and 18 show that gallium in large or small quantities is completely carried down when a considerable quantity of iron is present.

Expt. No.	Milligrams of gallium	Milliequivalents present			Minutes boiled	Precipitate
		$HC_2H_3O_2$	NH_4-$C_2H_3O_2$	NH_4Cl		
1	1	6	39	0	2	None, even on boiling 7 min.
2	1	6	39	30	7	None
3	2.5	6	39	6	2	Opalescent; fine ppt. after boiling 5 min. more.
4	20	6	39	30	2	Large; no Ga in filtrate.[a]
5	1	12	33	30	7	None; very small ppt. on adding 50 cc. of water and boiling.
6	2	6	39	30	7	Small.
7	1	18	27	18	3	Opalescent; on longer boiling film formed on side of vessel.
8	1	18	27	*18	10	Turbidity.
9	2	18	27	18	5	Finely divided; coagulated on standing 5 min.
10	1	30	15	30	10	None.
11	2.5	30	15	30	4	Finely divided.
12	2.5	42	3	42	10	Opalescent.
13	1	12	3	*12	5	Turbidity; did not coagulate.
14	1	12	18	*12	3	Small; pption. seemed complete after boiling 6 min.
15	1	6	9	6	2	Small ppt., increased on boiling 3 min. more.
16	1	6	9	*6	2	Small; same as in Expt. 14.
17	20 300 Fe	6	39	30	2	Large; no Ga or Fe in filtrate.[a]
18	1 300 Fe	6	39	30	2	Large; no Ga or Fe in filtrate.[a]
19	2.5	6	0	6	5	None.
20	2.5	6	3	6	2	Pption. apparently complete.
21	2.5	6	9	6	2	Pption. more rapid than in Expt. 20.
22	2.5	6	24	6	2	Small; pption. after boiling 5 min. seemed complete.
23	2.5	6	39	6	2	Opalescent; fine ppt. after boiling 3 min. more.
24	2.5	6	54	6	5	None, even after standing several hours.
25	2.5	2	3	6	2	Ppt. after 10 sec.
26	2.5	6	9	6	2	Ppt. after 30 sec.
27	2.5	10	15	6	2	Ppt. after 1 min.
28	2.5	20	30	6	2	Small, fine.
29	2.5	30	45	6	2	None.

Experiments 19–24 show that too large an amount of acetate relative to the amount of $HC_2H_3O_2$ present decreases the delicacy of the precipitation, and that the most favorable conditions are with a ratio of $HC_2H_3O_2$ to $NH_4C_2H_3O_2$ of about 2/3. This corresponds to a H^+ concentration of approximately 0.000013 n.

To determine whether, while keeping this ratio constant, variation of the actual concentration of these two substances has any effect, experiments 25–29 were made. The volume in each case was 100 cc., and the solution was boiled for 2 minutes and then allowed to cool. It is seen that, the smaller the amounts of $HC_2H_3O_2$ and $NH_4C_2H_3O_2$ present, the more delicate the precipitation is for small amounts of gallium. However, in order to regulate the H^+ concentration during precipitation considerable quantities of the substances must be present or the buffer action is lost.

P. 92, N. 5.—Behavior of Gallium Alone and in the Presence of Iron, Aluminum, Manganese, Cobalt, or Zinc, with Ammonium Hydroxide and Sulfide.—A solution containing 50 mg. of Ga as $Ga(NO_3)_3$ and 5 cc. of 6 n. HCl was neutralized with 6 n. NH_4OH, and an excess of 3 cc. added; the mixture was heated to boiling, colorless $(NH_4)_2S$ was added till the vapors in the flask blackened lead acetate paper; the mixture was heated nearly to boiling, shaken, and filtered; the filtrate was tested for gallium: it contained about half of the gallium.

The experiment was repeated with 25 mg. of Ga: the precipitate contained only 2 or 3 mg. of Ga.

The behavior of 25 mg. of Ga in the presence of other elements was also determined. The results are summarized in the following table.

Element	Fe	Al	Al	Mn	Co	Zn	Zn	Zn
Milligrams taken	300	100	25	300	300	300	50	25
Mg. of Ga in precipitate	25	25	5–10	25	25	25	25	15
Mg. of Ga in filtrate	0	0	15–20	0	0	0	0	10

P. 92, N. 5.—Behavior of Vanadium, Alone and with Other Elements, with Ammonium Hydroxide and Sulfide.—The results of N–B–S (pages 524–529, 537–538) in experiments similar to those just described are summarized below. The valence stage of the iron and vanadium in the salts used is shown by Roman affixes (II, III . . .).

Milligrams taken	20 V^V	25 V^{IV}	100 V^{IV} 500 Fe^{II}	10 V^{IV} 500 Fe^{III}	100 V^V 200 Mn^a	10 V^V 300 Zn
Cc. of solution	100	100	40	40	100	30
Mg. of V in precipitate	0	0	—	—	—	6–7
Mg. of V in filtrate	20	25	0.5–1.0	0	2–3	3–4

[a] 100 mg. of Zn and 100 mg. of U were also present in this experiment.

In the following experiments of N–B–S no $(NH_4)_2S$ was added.

Milligrams taken.....	50 V^{IV}	100 V^{V} 500 Fe^{II}	100 V^{V} 500 Fe^{III}	15 V^{IV} 50 Fe^{III}	15 V^{IV} 50 Fe^{III}	50 V^{V} 250 U
Cc. of solution	100	40	40	100	100	30
Mg. of V in filtrate.....	50	0	<0.1	<0.1	0	1

P. 92, N. 6.—Co-Precipitation by Ammonium Hydroxide of Zinc, Nickel, or Cobalt, with Titanium, Zirconium, Iron, or Aluminum.—See C. E., D. 96.

P. 92, N. 7.—Effect of Phosphate on the Precipitation of the Colloidal Cerium-Iron Mixture in the Acetate Treatment.—See C. E., P. 92, N. 2–8, Expt. 21, in which the milliequivalents present were 16.1 Fe, 2.11 Ce, 7.26 PO_4, so that the ratio of equivalents of PO_4 to those of Ce was 3.4. Here all of the cerium and iron were precipitated.

The following experiment was made to determine the minimum amount of phosphate necessary to ensure the coagulation of the iron-cerium colloid. A solution containing in 100 cc. 300 mg. of Fe and 100 mg. of Ce as nitrates (equal to 16.1 and 2.11 milliequivalents), and 6, 39, and 30 milliequivalents of $HC_2H_3O_2$, $NH_4C_2H_3O_2$, and NH_4Cl, respectively, was heated to boiling: there was no precipitate in the red solution. ½ cc. of 1 n. Na_2HPO_4 was added: some precipitation ensued, but it was far from complete. The mixture was boiled for two minutes, and filtered; to the red filtrate ½ cc. of 1 n. Na_2HPO_4 was added, the mixture was boiled for two minutes: the filtrate was still red, showing that the precipitation of iron is still incomplete when the ratio of equivalents of PO_4 to Ce is about ½. A third ½-cc. portion of the phosphate solution was added, and the large precipitate that formed was filtered off: the filtrate was slightly yellow. It was boiled for 2 minutes, and filtered: the precipitate contained only a few milligrams of iron. The colorless filtrate was made alkaline with NH_4OH: a white precipitate separated, which contained 5–10 mg. of Ce and no iron. In this experiment the ratio of equivalents of PO_4 to those of Ce, which was equal to 3/4, was sufficient to bring about coagulation of the colloid, and to cause complete precipitation of the iron, but not of the cerium.

P. 93, N. 1.—Behavior with Hydrochloric Acid of the Hydroxides of Titanium and Zirconium.—N–B–S, 540, show that $TiO(OH)_2$ and $ZrO(OH)_2$ dissolve rapidly in 6 n. HCl when freshly precipitated at room temperature, but only slowly when precipitated at 100°.

25 mg. of Zr as $ZrO(NO_3)_2$ in HNO_3 solution were heated to fuming with 1 cc. of 36 n. H_2SO_4, added to 6 cc. of water, and precipitated by adding 7 cc. of 6 n. NH_4OH; the mixture was heated to boiling, and

at once acidified with 6 n. H_2SO_4, an excess of 1 cc. being added; the mixture was heated just to boiling, and allowed to cool slowly: the precipitate dissolved rapidly during the heating, and the solution was almost clear in 3 minutes and became entirely so on again heating it to boiling.—The experiment was repeated, except that the alkaline mixture, after it had been heated to boiling, was kept on a steam-bath for about 3 hours: on acidifying and heating to boiling about three fourths of the precipitate dissolved; after 15 minutes' standing the precipitate still contained about 2 mg. of Zr, and the solution was almost clear only after 4 or 5 hours.

P. 93, N. 2, 3.—Extraction of Ferric and Gallium Chlorides by Ether. —As to $FeCl_3$ see Rothe, *Stahl und Eisen*, **12**, 1052 (1892), **13**, 333 (1893); N–B–S, 558. As to $GaCl_3$ see Swift, *J. Amer. Chem. Soc.*, **46**, 2375 (1924).

Behavior of Various Other Elements upon Shaking their Hydrochloric Acid Solutions with Ether.—By Swift, *loc. cit.*, 2378, results are tabulated and references given for 37 elements, including all the members of the Aluminum, Nickel, and Zirconium Groups and four members of the Rare-Earth Group. The results of Wada and Ato on indium and the experiments which were made with other elements of these four groups as a part of the investigation of this System of Analysis are reproduced here, as follows:

In 4 separate experiments 1, 10, 30, and 50 mg. of In as $InCl_3$ in 10 cc. of 6.5 n. HCl were shaken with 3 successive 10-cc. portions of ether: the total amounts of indium extracted by the ether were determined (by evaporation, addition of water and HCl, and precipitation of $In(OH)_3$ by NH_4OH) to be 0, 0.3, 0.7, and less than 1 mg., respectively.—The experiment was repeated with 3 mixtures: 1 mg. of In as $InCl_3$ with 100 mg. of Fe as $FeCl_3$, 1 mg. of In with 100 mg. of Tl as $TlCl_3$, and 2 mg. of In with 100 mg. of Fe and 100 mg. of Tl: the $FeCl_3$ and $TlCl_3$ were removed in the 3 extractions, and practically all the $InCl_3$ remained in the aqueous layer.

100 mg. of Th, 100 mg. of Ce, 100 mg. of Y, and 30 mg. of Sc as chlorides were in separate experiments dissolved in 50 cc. of 6.7 n. HCl; shaken with 50 cc. of ether; and the ether layer was tested by evaporation, addition of dilute HCl and NH_4OH: the precipitates that formed on standing corresponded to only about 0.2 mg. of Th, Ce, and Y, and 0.1 mg. of Sc.

A solution of 100 mg. of V as Na_3VO_4 in 10 cc. of 6 n. HCl was shaken twice with 10 cc. of ether, which had been previously shaken with twice its volume of 6 n. HCl; the combined ether extracts were evaporated to dryness, the residue was dissolved in HNO_3, tested

with H_2O_2 (as in P. 106, 3d paragraph), and the colors compared with standards: the amount of vanadium was estimated to be 1–2 mg. —The experiment was repeated, except that the Na_3VO_4 solution in HCl was first evaporated to 1 cc., as directed in P. 93: the solution had a greenish-blue color, showing that the vanadium had been reduced to the quadrivalent state, though perhaps not completely; the combined ether extracts contained about 1 mg. of V; and the combined ether layers from two additional treatments contained 0.7 mg. of V.

50 mg. of Be as pure $BeCl_2$ in 12 cc. of 7 n. HCl were extracted with three 12-cc. portions of ether: the united ether layers on evaporation and treatment with water, HCl, and a small excess of NH_4OH gave no precipitate.

100 mg. of W as Na_2WO_4 and 100 mg. of PO_4 as Na_2HPO_4 in HCl solution were evaporated just to dryness, dissolved in 12 cc. of 7 n. HCl, and extracted with three 12-cc. portions of ether: on the addition of ether a large white precipitate formed, but remained in the water layer. (After the experiment it was filtered off and found to contain about 60 mg. of W and 2 mg. of PO_4.) The united ether extracts were evaporated, and 5 cc. of 6 n. HCl were added. A portion of the clear solution was tested for PO_4 with molybdate; no precipitate formed. The remainder was tested for tungsten with $SnCl_2$ by P. 36: the small blue precipitate obtained corresponded to not more than 0.3 mg. of W in the combined ether extracts.

P. 94, N. 1.—Reduction of Ferric Chloride by Mercury and Non-Extraction of Ferrous Chloride by Ether.—A solution of 500 mg. of Fe as $FeCl_3$ in 10 cc. of 6 n. HCl was shaken with 1 cc. of mercury in a small corked flask almost continuously for 5 minutes; a small portion was withdrawn, and tested with KSCN: by comparison with standards the amount of ferric iron in the 10 cc. of solution was estimated to be 0.1–0.2 mg.

The remainder of the solution was filtered and shaken with two 10-cc. portions of ether (which had been treated with 6 n. HCl): the total amount of iron found in the combined ether extracts was estimated to be only 0.1–0.2 mg., showing that little if any $FeCl_2$ was extracted from the 6 n. HCl in two ether treatments.

A slightly acid solution containing about 450 mg. of Fe as $FeCl_2$ in 10 cc. was prepared by treating 300 mg. of Fe as $FeCl_3$ with metallic Fe until after 8 minutes there was no test for ferric iron with KSCN; 10 cc. of 12 n. HCl were added, and the solution was shaken with 20 cc. of ether which had been previously treated with 6 n. HCl; the ether layer was evaporated, the residue was dissolved in water, and tested for iron with NH_4OH in excess and H_2S: there was a very

small precipitate corresponding to less than 0.1 mg. of Fe, which may have been due to ferric salt formed during the extraction.

P. 94, N. 2.—Separation of Iron and Gallium by Sodium Hydroxide Solution.—See Swift, *J. Am. Chem. Soc.*, **46**, 2379 (1924).

P. 94, N. 4.—Precipitation of Gallium, Zinc, and Iron as Ferrocyanide.—Three drops of a solution containing 0.5 mg. of Ga as $Ga(NO_3)_3$ were added to 3 cc. of 6 n. HCl and 10 cc. of water; 3 cc. of 1 n. $K_4Fe(CN)_6$ were added: a distinct turbidity formed in less than 1 minute, and after standing 5–10 minutes considerable flocculent precipitate had settled out. The precipitate and solution were slightly bluish-green, due partly to a trace of iron in the gallium solution, and partly to the decomposition of the ferrocyanide.—The above experiment was repeated, the acid being diluted with only 5 cc. of water. Under these conditions a distinct turbidity formed in 1–3 minutes.

In another experiment a precipitate containing 2½ mg. of Ga, which had been precipitated by an acetate treatment (P. 92), was treated on the filter with 3 cc. of cold 6 n. HCl, the filter being washed with 6 cc. of water; 2 cc. of 1 n. $K_4Fe(CN)_6$ were added to the 9 cc. of solution: a pronounced turbidity formed in 15–20 seconds and in 5 minutes a large voluminous and flocculent precipitate had begun to settle out.

To a solution containing 3 mg. of Zn in 3 cc. of 6 n. HCl, diluted with 10 cc. of water, were added 3 cc. of 1 n. $K_4Fe(CN)_6$: a large precipitate formed.—A similar result was obtained upon repeating the experiment and diluting with only 5 cc. of water.

A solution containing 0.3 mg. of Fe as $FeCl_3$ in 6 cc. of 6 n. HCl was diluted with 5 cc. of water, and 3 cc. of 1 n. $K_4Fe(CN)_6$ were added: a deep-blue color appeared at once, and a blue precipitate gradually settled.

To determine the effect of various quantities of iron the following experiments were made: To a test-tube containing 0.025 mg. of Fe as $Fe(NO_3)_3$ in 3 cc. of 6 n. HCl were added 5 cc. of water and 3 cc. of 1 n. $K_4Fe(CN)_6$, and the solution thoroughly shaken: a distinct bluish-green color developed in 10–20 seconds.—With 0.1 mg. of Fe the bluish color was distinctly darker, and was accompanied by a very fine precipitate, at first scarcely more than a turbidity.—With 0.3 mg. of Fe the blue color was so intense that the solution was almost opaque.—With 1 mg. of Fe an immediate opaque blue color developed, accompanied by a distinct precipitation.—The experiment was repeated with 0.1 mg. of Fe with 10 cc., instead of 5 cc., of water; there was no appreciable difference in the result.

Behavior of Aluminum with Potassium Ferrocyanide Solution.—To a solution containing 3 cc. of 6 n. HCl, 10 cc. of water, and 3 cc. of 1

n. $K_4Fe(CN)_6$ was added 1 cc. of a solution containing 50 mg. of Al as $Al(NO_3)_3$: no precipitate formed.

As to the separation of gallium from aluminum and beryllium by precipitation as ferrocyanide see Browning and Porter, *Am. J. Sci.*, (4), **44**, 221 (1917).

Recovery of Gallium from Ferrocyanide.—Porter and Browning, *J. Am. Chem. Soc.*, **43**, 111 (1921), state that gallium can be quantitatively precipitated and separated from ferrocyanide by saturating NaOH solutions with CO_2; but they do not state the NaOH concentration. The C. E. on P. 101, N. 4, indicate that if the NaOH solution is initially more concentrated than 0.2–0.3 n., the precipitation of the gallium is incomplete; in other words, a solution of $NaHCO_3$ saturated with CO_2 dissolves $Ga(OH)_3$ at room temperature when the $NaHCO_3$ solution is more concentrated than 0.2–0.3 f., or about 2%.

P. 94, N. 4.—Detection of Gallium in the Presence of Iron.—500 mg. of Fe as $Fe(NO_3)_3$ and 1 mg. of Ga as $GaCl_3$, in a solution containing in 100 cc. 5 cc. of 6 n. HCl and 3 cc. of 3 n. NH_4Cl, were precipitated as directed in P. 92; and the precipitate obtained was treated by P. 93 and P. 94: a precipitate of gallium ferrocyanide was obtained, showing that no appreciable amount of the gallium had been lost.

P. 94, N. 5.—Behavior of Thallium in the Process for the Detection of Iron and Gallium.—Oxidation to the trivalent state by bromine: see C. E., P. 62, N. 1.—Behavior in the acetate treatment (P. 92): see N–B–S, 558, showing that trivalent thallium is nearly completely precipitated when much iron is present, but not in its absence.—Extraction by ether (P. 93): see N–B–S, 559.—Reduction by H_2SO_3 and precipitation as TlI: see N–B–S, 561; and C. E., P. 63, N. 2.

P. 95, N. 2.—Precipitation of Zirconium and Rare-Earth Elements by Sodium Peroxide.—As to zirconium, see N–B–S, 540.

To 1 mg. of Y and 0.5 mg. of Sc in separate casseroles were added 20 cc. of water, a few drops of 6 n. NaOH, 2 cc. of Na_2O_2 powder, and 5 cc. of 10% Na_2CO_3 (see N–B–S, 499, 501), and the mixture was boiled for 6 minutes: in the yttrium solution a precipitate corresponding to about 0.3 mg. of Y separated, but in the scandium solution none could be seen. The scandium solution was, however, filtered, the filter was washed, 5 cc. of 6 n. HCl were poured through it, and the solution was made alkaline with 6 n. NH_4OH: a faint turbidity appeared at once, and on standing a small coagulated precipitate resulted.

Decomposition of Freshly Precipitated Phosphates of Titanium, Zirconium, and Thorium by Boiling Sodium Hydroxide Solution.—See C. E., P. 42, N. 2, as to the separation of phosphate from titanium or zirconium by NaOH solution.

In each of five experiments the phosphate, freshly precipitated from an acid solution, was added to 50 cc. of NaOH solution of the concentration given in the following table; the mixture was boiled for the stated time and filtered; the residue was washed until the wash-water was free from PO_4, and then treated with 6 n. HCl: the residue dissolved completely in each case. This HCl solution was tested for PO_4: the estimated milligrams of PO_4 are shown in the last column.

Milligrams of element	*NaOH*	*Time of boiling*	*HCl solution contained*
100 Ti	1 n.	5 min.	100 Ti and 0 PO_4
100 Ti	1 n.	2 min.	100 Ti and 3 PO_4
10 Zr	0.5 n.	4 min.	10 Zr and 0 PO_4
50 Th	3 n.	4 min.	50 Th and 0 PO_4
50 Th	3 n.	1 min.	50 Th and 2 PO_4

P. 95, N. 2–4.—Behavior of Cobalt, Chromium, Vanadium, and Uranium on Boiling with Sodium Peroxide Solution.—See N–B–S, 541, 543, as to the first three elements; and C. E., P. 97, N. 3, as to uranium.

P. 95, N. 5.—Decomposition of Sodium Peroxide by Boiling its Solution.—See N–B–S, 542.

P. 95, N. 5.—Precipitation of Indium by Sodium Hydroxide and Peroxide.—1 mg. of In as $InCl_3$ was dissolved in 15 cc. of water containing 2 cc. of 6 n. HCl, the solution was neutralized with 6 n. NaOH, and an excess was gradually added: with 0.2 cc. excess, a white precipitate appeared; this seemed to dissolve to some extent with 3 cc. excess, but at least half of it remained even with 6 cc. excess. Without dilution, the mixture was heated to boiling and cooled: the precipitate now seemed as large as at first.—To 1 mg. of In as $InCl_3$, in 25 cc. of cold water, was added 6 n. NaOH until the precipitate dissolved, about 10 cc. being required. The mixture was boiled: a white precipitate separated, corresponding to 1 mg. of In.

The following experiments are described by Wada and Ato, *Sci. Papers Inst. Phys. Chem. Research*, 1, 69 (1922).

In four separate experiments 1, 2, 5, and 10 mg. of In as nitrate in about 10 cc. of HNO_3 solution were treated by P. 95, 1 g. of Na_2O_2 and 5 cc. of 1 n. Na_2CO_3 being added, and the mixture boiled for 3 minutes to decompose the Na_2O_2; then diluted and filtered: no trace of indium was found in the filtrate.—In a similar experiment with a mixture of 500 mg. of Zn and 1 g. of In, no In was found in the filtrate.—The same experiment was repeated with a mixture containing 10 mg. of In, 50 mg. of Mn, and 50 mg. of PO_4 (as Na_2HPO_4): the In and Mn were completely precipitated.—The same experiment

was repeated with a mixture containing 2 mg. each of Al, Cr, Zn, Be, U, V, Fe, Mn, Tl, Zr, Ti, and In: analysis showed that the last 6 elements had precipitated completely, and that the first six had remained in solution.—The last experiment was repeated with 1 mg. of each of the same 12 elements: satisfactory tests were obtained except in the case of aluminum.

Incomplete Precipitation of Titanium by Boiling Sodium Peroxide Solution.—In the experiments of N–B–S, 540, when 500 mg. of Ti as chloride in HCl solution were treated with NaOH, Na_2CO_3, and Na_2O_2 and the mixture boiled, the filtrate was found to contain at least 5 mg. of Ti as peroxytitanate after vigorous boiling for one minute, and 1–2 mg. of Ti after boiling for 5 minutes.—In an experiment with 1 mg. of Ti precipitation was complete after 4 minutes' boiling, and the filtrate when acidified contained no H_2O_2.

To 100 mg. of Ti as chloride were added 20 cc. of water, 2 cc. of 6 n. NaOH, and 5 cc. of 10% Na_2CO_3: there was a large precipitate. 2 cc. of solid Na_2O_2 were added gradually to the cold mixture: the precipitate dissolved completely, showing that the titanium had been converted into peroxytitanate. The solution was boiled gently for 3 minutes, and filtered: the precipitate was later found to contain 63 mg. of Ti. The filtrate was heated on a steam-bath for 1 hour: only 31 out of the remaining 37 mg. of Ti precipitated, showing that the decomposition of the peroxytitanate is much less rapid on a steam-bath than when the solution is boiled.

The last experiment was repeated with 1 mg. of Ti as chloride: after 5 minutes' boiling the filtrate contained 0.2 mg. of Ti, as estimated from the color obtained on the addition of H_2O_2 to the acidified solution.—The experiment was repeated with 1 mg. of Ti and with 2 mg. of Ti: after 10 minutes' boiling the filtrates contained no titanium.

50 mg. of Ti as sulfate in HCl solution were treated by P. 95, 2 g. of Na_2O_2 and 5 cc. of 10% Na_2CO_3 being added, and the solution (of volume 25 cc.) was boiled for 5 minutes, and the precipitate was filtered off: this was found to contain 45 mg. of Ti. The filtrate (of volume 50 cc.) was boiled for 5 minutes, and filtered: the precipitate contained 5 mg. of Ti, and the filtrate now contained no titanium and no H_2O_2, showing that the titanium had been completely precipitated in the 10 minutes' boiling.

P. 95, N. 7.—Action of Boiling Sodium Hydroxide and Peroxide on Porcelain.—A solution of 2 cc. of dry Na_2O_2 in 20 cc. of water was boiled gently in a covered casserole for 5 minutes; then it was acidified with HCl, and treated with 6 n. NH_4OH, care being taken to add an excess of only 0.5–1 cc.: the precipitate corresponded in size but not

in appearance to that obtained with 1 mg. of Al. In a control test with 2 cc. of Na_2O_2 there was no precipitate with NH_4OH, even when the mixture was boiled gently for a few minutes.—The experiment was repeated with a casserole of another make: the result was almost the same.

A solution of 2 cc. of dry Na_2O_2 in 25 cc. of water was heated gently in a covered casserole for 5 minutes, boiled gently for 10 minutes, and tested as before: the precipitate corresponded in size to that with 2 mg. of Al.—In a similar experiment performed some years earlier, the precipitate corresponded to 5 mg. of Al.

Action of Sodium Peroxide Solution on Nickel or Platinum Vessels.—A solution of 2 cc. of dry Na_2O_2 in 20 cc. of water was boiled gently in a covered nickel crucible for 10 minutes; then the solution was acidified with HCl, and evaporated to dryness; to the residue were added 10 cc. of water, 3 cc. of 10% tartaric acid solution, enough 6 n. NaOH to neutralize it and then 2 cc. more, and the mixture was saturated with H_2S: a brown color resulted corresponding to 0.02 mg. of Ni.

A solution of 2 cc. of Na_2O_2 in 10 cc. of water was heated at or near the boiling-point for 5 minutes in a covered nickel crucible; the clear solution was neutralized with HCl, evaporated, and tested with dimethylglyoxime in a solution made slightly acid with $HC_2H_3O_2$: a faint pink color resulted, corresponding to less than 0.05 mg. of Ni.

The experiment was repeated, except that 20 mg. of Mn as $Mn(NO_3)_2$ were also present: the decomposition of the Na_2O_2 was very rapid. Without filtering it the mixture was acidified and the manganese removed by P. 121; the filtrate was evaporated and tested for nickel as before: no pink color could be seen.

These two experiments were repeated with the same results.

A solution of 2 cc. of Na_2O_2 in 20 cc. of water was heated in a platinum dish for 5 minutes; the solution was acidified with HCl, evaporated in a casserole to a small volume: a very faint yellow color was observed. A small portion of the solution was tested with KSCN: a little iron was found. The remainder, made 6 n. in HCl, was treated with ether (P. 93), and the aqueous layer was evaporated to dryness on a steam-bath: the residue was now colorless, showing that the amount of platinum present is negligible.

THE SULFIDE PRECIPITATE: PROCEDURES AND NOTES

P. 96, N. 1–4.—Behavior of Various Elements with Ammonium Hydroxide, and with Ammonium Hydroxide and Hydrogen Sulfide or Ammonium Sulfide.—See N-B-S, 532–6. Some of their results may be summarized as follows:—

0.5 and 1 mg. of Al, Be, U, Zr, ferrous Fe, Cr, and Ti in 35 cc. of solution containing 30 milliequivalents of NH_4Cl, in separate experiments, were treated with 1 cc. excess of 6 n. NH_4OH at room temperature: the solutions were transparent at first; but in each case a distinct flocculent precipitate was seen after the solution was shaken and allowed to stand a few minutes.

Similar experiments were made in a volume of 105 cc. with an excess of about 2 cc. of NH_4OH: the limit of detectability at room temperature after the shaking and standing was 1, 2, and 1–2 mg. of Al, Cr, and U, respectively; while after heating to boiling and standing a few minutes the limit was 0.5 mg. of Al and Cr and 1 mg. of U (as found in a new experiment described below). In the case of aluminum and chromium an excess of more than 2 or 3 cc. of 6 n. NH_4OH in 100 cc. of solution containing 30 milliequivalents of ammonium salt is to be avoided, but even then 0.5 mg. can be detected by boiling off some of the NH_3.

To separate solutions containing in 105 cc. small amounts of Mn, Zn, Co, ferrous Fe, Tl, and U and 30 milliequivalents of NH_4Cl, an excess of about 4 cc. of 6 n. NH_4OH was added, and then colorless $(NH_4)_2S$ solution drop by drop until an excess was present; the mixtures were well shaken and filtered; the filtrates were evaporated to a small volume, and tested for the element by methods which would have detected 0.1 mg. or less: distinct precipitates were obtained with $(NH_4)_2S$ at room temperature with 0.25 mg. of Mn, 0.5 mg. of Zn, 0.1 mg. of Co, 0.2 mg. of Fe, 0.3 mg. of Tl, and 0.3–0.5 mg. of U; showing that all these elements are completely precipitated.

In several experiments 500 mg. of Ni as $Ni(NO_3)_2$ were dissolved in 30 cc. of 1 n. HCl; 6 n. NH_4OH was added until the odor could be detected after shaking and then 3 cc. more, and H_2S was led into the mixture for 15 minutes: the precipitates were always granular, and the filtrates clear and colorless. The precipitates were washed with water containing either H_2S or a little $(NH_4)_2S$: the wash-water was clear.

New experiments were made as follows:—

1 mg. of In as $InCl_3$ in 100 cc. containing 5 cc. of 6 n. HCl was treated by P. 92, except that no $Fe(NO_3)_3$ was added; and the clear solution was treated by P. 96. When the excess of NH_4OH was added, a small white precipitate of $In(OH)_3$ separated, which seemed

to increase on heating. H_2S and heating apparently had no effect; but, after the mixture was cooled and the precipitate allowed to settle, it was observed to have a light-yellow color, showing that the $In(OH)_3$ had been converted into In_2S_3.—The experiment was repeated with 5 mg. of In: the precipitate became pale-yellow when a little H_2S was passed into the cold ammoniacal mixture.

To 1 mg. of Mn as $Mn(NO_3)_2$ in 100 cc. containing 3 cc. of 6 n. $HClO_4$, 2 cc. of 6 n. HCl, 4 cc. of 6 n. NH_4OH, and 15 cc. of 3 n. $NH_4C_2H_3O_2$ was added NH_4OH as in P. 96: the solution remained clear. H_2S was then passed in: a slight turbidity was observed, which on warming coagulated. The precipitate seemed to increase in size as the solution cooled, and it settled rapidly in the cold solution.

1 mg. of U as $UO_2(NO_3)_2$ in 100 cc. containing 3 cc. of 6 n. $HClO_4$ and 2 cc. of 6 n. HCl was treated by P. 92 except that no $Fe(NO_3)_3$ was added; and the clear solution was treated by P. 96: upon adding NH_4OH no precipitate could be seen in the cold, or on boiling. With H_2S in the cold there was a turbidity, which seemed to increase in size, especially when the mixture was heated to boiling; on long standing it settled out as a dark powder (see N–B–S, 535). This may have been either UO_2S or a mixture of UO_2 and S.—The experiment was repeated, except that the mixture was not heated after the addition of H_2S: the precipitate was smaller and did not settle as quickly. On analysis by P. 105 the two precipitates were estimated to contain 0.9 and 0.5 mg. of U respectively; showing that the precipitation of the uranium by sulfide is practically complete when the mixture is heated, and that 1 mg. of U can be detected in the cold.

To 2 mg. of U in 115 cc. of solution containing 30 milliequivalents of NH_4Cl and 39 of $NH_4C_2H_3O_2$ were added 2 cc. of 6 n. NH_4OH in excess: there was no precipitate in the hot solution after 2 minutes. 2 cc. more 6 n. NH_4OH were added: a slight turbidity appeared, and after 30 minutes' heating on a water-bath a small yellow precipitate had settled out.

A solution containing in 100 cc. 1 mg. of U as $UO_2(NO_3)_2$ and 30 milliequivalents of NH_4Cl was heated nearly to boiling, and 2 cc. excess of 6 n. NH_4OH were added: there was at once a distinct, white turbidity, which coagulated and settled as a small yellow precipitate in 5 minutes, indicating that the precipitation of uranium is somewhat more complete in the absence of $NH_4C_2H_3O_2$. (A similar conclusion can be drawn from the experiments with NH_4OH and $(NH_4)_2S$ at room temperature already described.)

The last experiment was repeated with 0.5 mg. of U: there was a barely perceptible turbidity in the hot solution in 5 minutes, but no yellow precipitate in 20 minutes.

P. 97, N. 3.—Behavior of Uranium on Boiling with Sodium Peroxide Solution.—50 mg. of U as $UO_2(NO_3)_2$ were treated by P. 97, 3 g. of Na_2O_2 being added; and the deep-red solution was boiled vigorously in an open casserole for 10 minutes: the solution remained clear for 9 minutes, during which time its volume had decreased from 25 cc. to about 10 cc., but became turbid in the next minute. The mixture was diluted and filtered: the precipitate was dissolved in HCl, treated with NH_4OH and H_2S (P. 96), and estimated to contain 6 mg. of U. The filtrate was found to contain much H_2O_2 by the titanium test, showing that the uranium was largely present as peroxyuranate.

The experiment was repeated except that the volume of the boiling solution was maintained at about 25 cc. by the addition of water at intervals: the solution remained clear for 5 minutes, and the precipitate at the end of 10 minutes' boiling contained about 25 mg. of U. The filtrate was diluted to 50 cc., and boiled for 6 minutes: no further precipitate separated. The solution was acidified: it was found to contain much H_2O_2. It follows from these experiments and those with titanium that some uranium precipitates if the NaOH solution is boiled long enough to complete the precipitation of a large amount of titanium.

A mixture of 50 mg. of U and 40 mg. of Fe as nitrates was treated by P. 97, 2 g. of Na_2O_2 being used; the mixture (25 cc.) was boiled for 10 minutes, diluted, and filtered; the precipitate was treated with cold Na_2O_2 to extract the uranium, and the $Fe(OH)_3$ was filtered off. The two filtrates were acidified, and treated with NH_4OH and H_2S to precipitate uranium: it was estimated that about half the uranium, 25 mg., had been carried down with the iron in the 10 minutes' boiling.—The experiment was repeated except that the mixture was boiled for only 1 minute: about 10 mg. of U were precipitated with the iron, showing that iron has a tendency to carry down uranium, possibly by acting as a catalyst for the decomposition of the peroxyuranate.

P. 97, N. 4.—Division of Zinc on Boiling with Sodium Peroxide Solution.—N–B–S, 522 (Test Analyses Nos. 140–143), show that a mixture of 250 mg of Ni and 250 mg. of Co carries down zinc in the Na_2O_2 treatment as follows: 3 mg. completely; 4 mg. out of 5 mg.; and, when 200 mg. of PO_4 were also present, 5 or 10 mg. completely or nearly so.—Experiments with manganese and with iron, N–B–S, 544, show that 500 mg. of Mn carries down 10 mg. of Zn completely, and at least 19.5 out of 20 mg.; and that 500 mg. of Fe carries down 5 mg. of Zn nearly completely, and 7 out of 10 mg.

Hufferd, *J. Am. Chem. Soc.*, 45, 438 (1923), claims that it is unnecessary to test for zinc in the precipitate when a large excess of sodium hydroxide has been used; but he does not specify the amount, nor does he refer to the work of Noyes, Bray, and Spear cited above.

ANALYSIS OF THE ALUMINUM GROUP

GENERAL DISCUSSION

D. 106.—Separation of Beryllium and Uranium by the Use of Hydroxylamine.—For the method proposed by Brinton and Ellestad, see *J. Am. Chem. Soc.*, **45**, 395 (1923). As to compounds of sexivalent uranium and hydroxylamine see Abegg, *Handbuch*, IV, 1 (2), 962; references are given to papers by Hofmann, Kohlschütter, and Friedheim (1897–1905). The solid compounds contain 2 NH_2OH per atom of uranium.

A mixture of 2 mg. of U and 100 mg. of Be as nitrates was treated by the two-stage process of Brinton and Ellestad; the hydroxylamine in the filtrate was destroyed (as they recommend) by acidifying with HCl, adding $KBrO_3$, and boiling; NH_4OH in small excess was then added: a small nearly white precipitate separated. This was collected on a filter and treated by P. 105: the dark-red color obtained in this test with $K_4Fe(CN)_6$ and the size of the NH_4OH precipitate corresponded to 2 mg. of U; showing that little or no uranium had been precipitated with the beryllium.

To a mixture of 1 mg. of U and 50 mg. of Be as nitrates in 25 cc. of water were added 5 cc. of 1 f. NH_2OHHCl and 5 cc. of 6 n. NH_4OH: a large precipitate formed, which had a yellowish tinge. The filtrate was acidified with HCl, $KBrO_3$ was added and the solution was boiled to destroy the hydroxylamine; NH_4OH was added to faint alkaline reaction: there was no precipitate (even when 1 g. of NH_4Cl was added). One fourth of the solution was acidified with $HC_2H_3O_2$, and $K_4Fe(CN)_6$ added: there was no red coloration. These results confirm the conclusion of Brinton and Ellestad that uranium is carried down with the $Be(OH)_2$ precipitated by NH_4OH, even in the presence of hydroxylamine.

Behavior of Vanadium, Aluminum, Iron, and Titanium with Ammonium Hydroxide in the Presence of Hydroxylamine.—10 mg. of V as $VOCl_2$, prepared by evaporating Na_3VO_4 with HCl, were dissolved in 30 cc. of water; about 2 g. of NaCl, a little HCl, and 10 cc. of 1 f. NH_2OHHCl were added; and the solution was made alkaline with NH_4OH: the blue solution became colorless, but there was no precipitate.—The experiment was repeated, except that 50 mg. of U as $UO_2(NO_3)_2$ were also present: again there was no precipitate. The NH_2OH was destroyed by acidifying the solution with HCl, adding liquid Br_2, and boiling; the solution was then made alkaline with NH_4OH: a greenish-yellow precipitate was formed, which became yellow after the mixture had stood for a day exposed to the air.—The last experiment was repeated with a mixture of 10 mg. of V, 50 mg.

of U, and 5 mg. of Be: the beryllium was precipitated as a white precipitate of $Be(OH)_2$ when the NH_2OH solution was made alkaline with NH_4OH.

To a solution which contained 10 mg. of U, 3 mg. of Fe as $Fe(NO_3)_3$, 3 mg. of Al as nitrate, 3 mg. of Ti as chloride, 5 mg. of V as Na_3VO_4, and a little HNO_3, was added NH_4OH in small excess; the precipitate was treated by P. 115. The residue after the chloroform treatment was dissolved in 5 cc. of 6 n. HNO_3, 5 cc. of 2 n. NH_2OHHCl were added, NH_4OH was added in small excess, and the precipitate was filtered off; the filtrate was acidified with HNO_3, boiled with liquid Br_2 to destroy the NH_2OH, and make alkaline with NH_4OH: a yellow precipitate formed, which was estimated to contain 10 mg. of U, and which also contained much of the vanadium.

The experiment was repeated with a mixture of 3 mg. each of Fe, Al, and Ti: a small white precipitate separated when NH_4OH was added in the final test for uranium. This was found to contain about 1.5 mg. of Ti.

The experiment was repeated with 3 mg. of Fe or $Fe(NO_3)_3$: the filtrate from the first NH_4OH precipitate contained no iron.

To a solution containing 3 mg. of Ti as chloride, 5 cc. of 6 n. HNO_3, and 5 cc. of 2 f. NH_2OHHCl there was added 6 n. NH_4OH, 1 cc. at a time to distinct alkaline reaction: a precipitate formed while the solution was still acid and remained after it was alkaline. The mixture was filtered, and the filtrate tested for titanium after the NH_2OH had been oxidized as before: it contained about 1.5 mg. of Ti.—The experiment was repeated with 1 mg. of Ti, instead of 3 mg.: a small precipitate formed while the solution was acid, but it dissolved completely within 20 minutes at room temperature in the ammoniacal solution.—The experiment with 3 mg. of Ti was repeated, except that the NH_4OH was added all at once: there was no precipitate, showing that the final NH_4OH-NH_2OH solution contained 3 mg. of Ti.

ALUMINUM GROUP: PROCEDURES AND NOTES

P. 101, N. 1.—Oxidation of Chromium Hydroxide by Hydrogen Peroxide in Presence of Sodium Hydrocarbonate.—To 10 mg. of Cr as $Cr(NO_3)_3$ in HNO_3 solution was added NaOH solution: a precipitate of $Cr(OH)_3$ formed. HNO_3 was added until the solution was distinctly acid, but without dissolving much of the $Cr(OH)_3$. The mixture was diluted to 100 cc., and 1.5 g. of $NaHCO_3$ and 1 cc. of H_2O_2 were added, and the pressure-bottle was heated for 30 minutes and shaken twice during this time: within 2 or 3 minutes the solution was distinctly yellow, but the precipitate did not dissolve completely in the 30 minutes treatment. The mixture was cooled and filtered: the precipitate contained 3 mg. of Cr as $Cr(OH)_3$; and the filtrate contained 7 mg. of Cr as chromate, but no H_2O_2.

10 mg. of Cr as $Cr(NO_3)_3$ were treated with NaOH and Na_2O_2 by P. 95, and the clear yellow solution was treated as above. When the 1 cc. of H_2O_2 was added (after the 1.5 g. of $NaHCO_3$), the slight purple color of the solution showed that some peroxychromic acid had formed; this color disappeared when the pressure-bottle was warmed, but there was no evidence of reduction to trivalent chromium. After the 30 minutes' heating there was a small white precipitate, which was found to contain $Al(OH)_3$ and silica (from the NaOH reagent), but no chromium. The yellow chromate solution contained no H_2O_2; this shows that the decomposition of H_2O_2 in $NaHCO_3$ solution is catalyzed by the presence of chromate, since in a blank experiment with no chromium much H_2O_2 remained undecomposed.

P. 101, N. 2, 3.—Behavior of Various Elements with Sodium Hydrocarbonate Solution.—See N–B–S, 546–50, as to the precipitation of zinc and beryllium as carbonates and of aluminum as $Al(OH)_3$ (on p. 546, 8th line from bottom, change mg. to g.); as to the dissolving of beryllium at high concentrations of $NaHCO_3$; as to the precipitation of uranyl vanadate at low concentrations of $NaHCO_3$; and as to the non-precipitation of uranyl chromate, phosphate, or oxalate.—See also C. E., P. 116, N. 2.

A mixture of 100 mg. of U as $UO_2(NO_3)_2$ and 100 mg. of V as Na_3VO_4 was treated by P. 95 and 101, an excess of 1.5 g. of $NaHCO_3$ being used: no precipitate formed on the addition of the $NaHCO_3$ to the cold acid solution (which contained H_2O_2 from the peroxyuranate) and a clear yellow solution resulted after the 30 minutes' heating in the pressure-bottle. This was acidified and shown to contain some H_2O_2 by the titanium test.—The experiment was repeated, except that the addition of 1 cc. of 1 f. H_2O_2 after the $NaHCO_3$ was omitted: no precipitate formed in the $NaHCO_3$ solution, but no peroxide was found.

A mixture of 100 mg. of U as $UO_2(NO_3)_2$ and 100 mg. of V as Na_3VO_4 was treated directly by P. 101: a large yellow precipitate formed at once on the addition of $NaHCO_3$, and remained after the 30 minutes' heating in the pressure-bottle. While the initial precipitation in the cold solution may have been due mainly to the absence of H_2O_2 (see preceding experiments), the absence of $NaNO_3$ (that would have been formed in P. 95 and 101) is probably responsible for the fact that the uranyl vanadate did not dissolve to a greater extent during the pressure-bottle treatment.

As to the precipitation of uranium with aluminum or beryllium by sodium hydrocarbonate, see N–B–S, 523, test analyses 166–170.

A mixture of 200 mg. of Al and 10 mg. of U as nitrates was treated by P. 95 and 101, and the filtrate was tested for uranium by P. 104 and 105: only about 1 mg. of U was found, showing that the remaining 9 mg. had been carried down by the aluminum. The $NaHCO_3$ solution after the 30 minutes heating still contained some peroxide, shown by the titanium test in a small portion of the solution after acidifying.—The experiment was repeated, except that the presence of peroxide was completely avoided by omitting P. 95 and not adding H_2O_2 in P. 101: the $NaHCO_3$ solution was found to contain only about 1 mg. of U, as before.

P. 101, N. 4.—Behavior of Titanium with Sodium Hydrocarbonate Solution in the Presence of Hydrogen Peroxide.—A solution containing 10 mg. of Ti as chloride, HCl, and 0.5 cc. of 1 f. H_2O_2 was treated by P. 101: when the 1.5 g. excess of $NaHCO_3$ was added, a clear yellow solution resulted, which was not changed on the addition of the 1 cc. of 1 f. H_2O_2; on heating the solution in a pressure-bottle, a precipitate formed rapidly. After heating 30 minutes the cream-white precipitate was filtered off, and the colorless filtrate tested for Ti and H_2O_2: there was less than 0.3 mg. of Ti and only a trace of H_2O_2.

In a similar experiment a solution containing 10 mg. of Ti as chloride, 2 cc. of 6 n. NaOH and 0.5 cc. of solid Na_2O_2 in 40 cc. was acidified with HNO_3, diluted to 100 cc., and treated by P. 101; after 25 minutes' heating, the pressure-bottle was cooled, the fine, granular precipitate was filtered off, the filtrate was acidified and tested with H_2O_2: the amount of Ti was estimated to be 0.5 mg. Since, in the absence of H_2O_2, titanium is not dissolved by a dilute $NaHCO_3$ solution (cf. C. E., P. 116, N. 2), and since an abnormally large amount of peroxide was initially present in the $NaHCO_3$ treatment in this experiment, it is concluded that the amount of titanium that will enter the aluminum group will never exceed 0.5 mg., and will usually be much smaller.

P. 101, N. 4.—Behavior of Gallium with Sodium Hydrocarbonate Solution.—To 100 cc. of a slightly acid solution containing 50 mg. of Ga as $Ga(NO_3)_3$ and about 50 milliequivalents of $NaNO_3$, $NaHCO_3$ was added, and the mixture was heated in a pressure-bottle for 25 minutes, as described in P. 101: in the cold 1.5% $NaHCO_3$ solution (which must have been nearly saturated with CO_2), a large precipitate formed, some of which dissolved when the mixture was heated; when the bottle was opened at about 50° much CO_2 escaped. The $NaHCO_3$ filtrate was acidified and treated by P. 92 to precipitate the gallium: it was estimated that the $NaHCO_3$ precipitate contained 30 mg. of Ga, and the filtrate from it 20 mg.

In a series of experiments 2.5 mg. of Ga as $Ga(NO_3)_3$ were dissolved in 50 cc. of NaOH solution of various concentrations, and the solutions were completely saturated with CO_2: the precipitation was complete when the NaOH was 0.06 or 0.12 n.; with 0.36 n. NaOH there was a very small precipitate, which increased on adding 1 cc. of 6 n. HCl; and with 1.2 n. NaOH there was only a slight turbidity, but upon adding 6 cc. of 6 n. HCl a small precipitate formed, and with 8 cc. there was apparently complete precipitation. This would correspond to an initial NaOH concentration of 0.02 n.

In another series of experiments 20 mg. of Ga were in each case dissolved in 50 cc. of NaOH of the concentration given in the table, and the solution was completely saturated with CO_2; the precipitate was filtered out, dissolved in HCl, reprecipitated by an acetate treatment (P. 92), and estimated by comparison with standards; the filtrate was again saturated with CO_2 and examined for further precipitate, then a slight excess of HCl added, the CO_2 expelled by boiling, and the gallium precipitated by an acetate treatment (P. 92), and compared with standards. The amount of gallium precipitated upon saturating the original NaOH solution and the amount obtained from the filtrate are shown in the following table. In the last experiment a large precipitate of $NaHCO_3$ separated.

Normality of NaOH	0.2	0.3	0.6	1.0	2.0
Gallium in precipitate	20	19	17½	10–12	10–13 mg.
Gallium in filtrate	0	1	2½	10– 8	10– 7 mg.

P. 102, N. 1.—Incomplete Decomposition of Hydrogen Peroxide in the Sodium Hydrocarbonate Treatment.—The decomposition may be incomplete when uranium and vanadium are present (see N–B–S, 550), but is complete when chromium is present (see C. E., P. 101, N. 1).

P. 102, N. 3.—Behavior of Chromate, Vanadate, and Uranate with Lead Nitrate.—See N–B–S, 550–551, for the precipitation of lead

chromate in dilute HNO_3, and the non-precipitation of lead vanadate or lead uranate.

To a cold solution containing in 100 cc., 20 cc. of 1 n. $Pb(C_2H_3O_2)_2$, 25 cc. of 1 n. $Pb(NO_3)_2$, 1 g. of $NaNO_3$, 2.0 cc. of 6 n. HNO_3, and 1.8 cc. of 6 n. NH_4OH there were added 100 mg. of U as $UO_2(NO_3)_2$ in 10 cc.: no precipitate appeared in 30 minutes, showing that lead uranate does not precipitate in this very weakly acid solution. 1 mg. of V as Na_3VO_4 was then added, and the mixture was shaken immediately: a pale yellow flocculent precipitate formed quickly and remained for an hour; when filtered off, dissolved in HNO_3, and tested by P. 106, a very good test for vanadium was obtained, showing that lead vanadate can be completely precipitated in an acetic acid solution in the presence of a large excess of acetate. To the filtrate 1 mg. of W as Na_2WO_4 was added, and the mixture shaken at once: a small flocculent precipitate formed, which did not settle rapidly; when filtered off after 1 hour, and tested with $SnCl_2$ by P. 36, a satisfactory test for tungsten was obtained, showing that lead tungstate can be completely precipitated under these conditions.

P. 102, N. 5.—Precipitation of Lead Phosphate in Presence of Nitric Acid.—To a neutral solution, which contained in 100 cc. about 200 mg. of PO_4 as Na_2HPO_4 and 2 g. of $NaNO_3$, were added 2 cc. of 6 n. HNO_3 and 25 cc. of 1 n. $Pb(NO_3)_2$ as in P. 102: a white finely crystalline precipitate of $Pb_3(PO_4)_2$ of medium size separated, showing that some phosphate is precipitated when much is present. The mixture was boiled and 2 cc. of 6 n. HNO_3 were added: the precipitate did not dissolve.

P. 102, N. 6.—Behavior of Vanadium with Bromine and Hydrobromic Acid.—As to the oxidation of quadrivalent vanadium by Br_2 in dilute acid solution see N–B–S, 551. It was found, however, that vanadic acid is reduced by concentrated HBr.

P. 103, N. 1.—Test for Chromate with Hydrogen Peroxide.—See N–B–S, 545. As to peroxychromic acids see Riesenfeld, *Ber. d. chem. Ges.*, 38, 1885, 3380, 3578, 4068 (1905).

To determine the effect of having the chromic acid present in excess, a solution containing 10 mg. of Cr as K_2CrO_4 in 10 cc. of 0.6 n. HNO_3 was placed in a test-tube with ether, and 1 f. H_2O_2 was added, without shaking, a drop or two at a time: the first drop gave a faint bluish tint to the ether layer, but this disappeared rapidly when the upper portion of the mixture was gently stirred. Two drops were then added: a distinct blue color appeared at the top of the aqueous layer, and on gently stirring the upper portion of the mixture, the ether layer became blue; but when the mixture was shaken vigorously the blue

color disappeared. With 2 drops more the same result was obtained, and after vigorous shaking the aqueous layer was still orange and the ether layer colorless. Finally, when a small excess of H_2O_2 was added, the ether layer was deep blue after vigorous shaking, and the aqueous layer had only a faint green tint.

P. 103, N. 3.—Extraction of Lead Chromate by Nitric Acid or Ammonium Acetate from Precipitates containing also Other Lead Salts.— In each of several experiments 1 mg. of Cr as K_2CrO_4 and 100 mg. of SO_4 as Na_2SO_4 were precipitated with $Pb(NO_3)_2$ in the presence of HNO_3 as directed in P. 102; the precipitate which always had a distinct yellow color, was collected on a filter, and washed with water; a reagent was then poured repeatedly through the filter, and the amount of chromate dissolved by it was estimated from the color of the solution, with results as follows: practically no chromate was dissolved by 10 cc. of 0.6 n. HNO_3, whether cold or hot. With 11 cc. of hot 2.2 n. HNO_3 the precipitate on the filter became paler yellow, and the solution contained about 0.3 mg. of Cr; but on neutralizing about half of the HNO_3 with NH_4OH a heavy pale-yellow precipitate formed, and the solution was almost colorless.—With 15 cc. of hot 3 n. NH_4-$C_2H_3O_2$ much of the precipitate dissolved, the hot solution was yellow; but, on cooling, a yellow precipitate formed, which was collected on the filter; the cold $NH_4C_2H_3O_2$ solution then had only a slight yellow color, corresponding to less than 0.2 mg. of Cr. The small bright-yellow precipitate left on the filter was treated with 0.6 n. HNO_3 by pouring a cold 10 cc. portion repeatedly through the filter: the color of the precipitate did not change, and the solution had only a slight yellow color, corresponding to not more than 0.2 mg. of Cr.

The last experiment (with 3 n. $NH_4C_2H_3O_2$) was repeated, and the yellow precipitate was treated with 10 cc. of cold 1.2 n. HNO_3 (instead of 0.6 n.): the precipitate dissolved almost completely, and the solution contained about 0.7 mg. of Cr. This was diluted to 20 cc. and shaken with ether and H_2O_2: the ether became deep-blue.

A solution containing in 100 cc. 1 mg. of Cr as K_2CrO_4, 200 mg. of PO_4 as Na_2HPO_4, and 2 g. of $NaNO_3$ was treated with $Pb(NO_3)_2$ in the presence of HNO_3 as directed in P. 102: there was a large precipitate, showing that a considerable quantity of $Pb_3(PO_4)_2$ had separated; the precipitate had an intense yellow color. A hot 10 cc. portion of 0.6 n. HNO_3 was poured repeatedly through the filter: some of the precipitate dissolved, but the remainder was yellow and the solution was almost colorless. Enough 6 n. HNO_3 was added to make the solution 1.2 n. in HNO_3, and the extraction was repeated: nearly all of the precipitate dissolved, and the solution was yellow. The latter was tested with H_2O_2 as in P. 103: it gave a satisfactory result.

The experiment was repeated, except that 100 mg. of SO_4 as Na_2SO_4 were also present. The pale-yellow precipitate was treated first with 15 cc. of 3 n. $NH_4C_2H_3O_2$, and then with 10 cc. of 1.2 n. HNO_3, each reagent being poured 3 or 4 times through the filter: the precipitate was still yellow, and the HNO_3 solution was almost colorless. The yellow residue was transferred to a casserole, heated with 15 cc. of 3 n. $NH_4C_2H_3O_2$ nearly to boiling for 2 minutes, cooled, filtered, and then treated with 10 cc. of 1.2 n. HNO_3: the filtrate was slightly yellow, but did not contain more than 0.2 mg. of Cr; the confirmatory test with H_2O_2 failed. The yellow residue on the filter was treated a third time with 15 cc. of $NH_4C_2H_3O_2$: the small yellow residue now dissolved to a considerable extent in the 1.2 n. HNO_3, giving a yellow solution which contained 0.3–0.4 mg. of Cr; in the confirmatory test with H_2O_2 there was a faint-blue color in the ether layer.

P. 104, N. 1, 2.—Behavior with Phosphate of Uranium, Vanadium, Aluminum, Beryllium, and Lead.—See N–B–S, 551–552. As to the transformation of uranyl ammonium vanadate into phosphate see N–B–S, 552. As to the precipitation of uranyl hydrogen phosphate see Kern, *J. Am. Chem. Soc.*, **23**, 705 (1901).

P. 105, N. 1.—Behavior of Uranyl Salts with Potassium Ferrocyanide.—In each of the experiments tabulated below 5 cc. of 1 n. $K_4Fe(CN)_6$ were added to a solution of $UO_2(NO_3)_2$ in various volumes of 6 n. HCl and 10 cc. of saturated NaCl. The times after the addition of the $K_4Fe(CN)_6$ that elapsed before a color or turbidity or coagulation of the precipitate was observed are recorded in the tables.

With 1 mg. of U

Cc. of 6 n. HCl added	1	0.5	0.2	0.1	0
Dark-red color in	0	0	0	0	0 min.
Turbid in	1	1	5	5	30 min.
Coagulated in	5	5	30	30	60 min.
Precipitate settled in	15	30	60[a]	60[a]	— min.

With 0.5 mg. of U

Cc. of 6 n. HCl added	0.2	0	*b*
Dark-red color in	0	0 min.	No red color.
Turbid in	20 min.	— min.	—
Coagulated in	120 min.	150 min.	—

With 0.2 mg. of U

Cc. of 6 n. HCl added	5	2	1	0.5	0.2
Dark-yellow color in	—	0	0	0	0 min.
Red color in	—	3	½	½	½ min.
Turbid in	45[c]	3	3	10	120 min.

a Settled only partially. *b* The solution was made faintly alkaline with NaOH

With 0.1 mg. of U

Cc. of 6 n. HCl added	1	0.5	0.2
Red color in	2[d]	2	5 min.
Turbid in	2[d]	10	120 min.

[c] Very slight turbidity. [d] Slight turbidity with reddish tinge.

The experiment with 1 mg. of U and 0.5 cc. of 6 n. HCl was repeated, except that water was added instead of NaCl solution: the dark-red solution was still clear after one hour.

For evidence that the test is less delicate at lower concentrations of $K_4Fe(CN)_6$, see N–B–S, 552. The results of N–B–S are consistent with the preceding ones, except that in the eighth line from the bottom of p. 552 "precipitates separated" should read "colors appeared."

P. 105, N. 2.—Behavior of Titanium and Vanadium with Potassium Ferrocyanide in the Uranium Test.—5 cc. of 1 n. $K_4Fe(CN)_6$ were added to solutions of known amounts of titanium as sulfate dissolved in 0.2–1 cc. of 6 n. HCl and 10 cc. of saturated NaCl: each solution became orange-yellow at once; this color being very faint with 0.1 mg. of Ti, and decreasing (for constant amounts of titanium) with increasing concentration of acid. Each solution remained clear for the time in minutes recorded in the following table. After a turbidity appeared, the orange-yellow precipitate remained completely suspended for about 30 minutes.

Mg. of Ti	1	0.5	0.5	0.5	0.2	0.1
Cc. of 6 n. HCl	0.2	0.2	0.5	1	0.2	0.2
Remained clear	1	10	15	>15	>60	>60 min.
Slightly turbid in	2	15	20	<60	—	— min.

The experiment was repeated with a mixture of 0.5 mg. of Ti and 0.1 mg. of U, 0.2 cc. of 6 n. HCl being used: the orange-yellow color due to titanium appeared at once; a faint-red tinge in 1 minute and a deeper red in 2 minutes corresponded to 0.1 mg. of U alone; the solution became turbid in 10 minutes; the precipitate remained suspended for at least 30 minutes, but settled out in less than 2 hours. Its color before and after settling was intermediate between that of the precipitates obtained with titanium and uranium alone.

5 mg. of V as Na_3VO_4 were treated by P. 105: during the evaporation with HCl the color change showed reduction of vanadium to the quadrivalent condition; when the $K_4Fe(CN)_6$ solution was added, a greenish-yellow precipitate separated. For evidence that this precipitation of vanadium as vanadyl ferrocyanide is almost complete, and that quinquivalent vanadium in small amount is not precipitated by ferrocyanide, see N–B–S, 553.

5, 1, and 0.5 mg. of U as $UO_2NH_4VO_4$ (precipitated by NH_4OH as in P. 116) were treated by P. 105: on the addition of $K_4Fe(CN)_6$ there formed at once a dark-red precipitate in the experiment with 5 mg. and with 1 mg. of U, and a dark-red color in that with 0.5 mg. of U; in the last case a dark-red precipitate began to separate after about 1 minute.

P. 105, N. 2.—Separation of Uranium from Beryllium by Potassium Ferrocyanide.—15 mg. and 25 mg. of Be as $BeCl_2$ were as in P. 105 evaporated almost to dryness, 10 cc. of saturated NaCl solution were added, the mixture was cooled and 5 cc. of 10% $K_4Fe(CN)_6$ solution were added: clear solutions resulted which were blue, owing to the presence of a small amount of iron in the beryllium. The mixtures were let stand several hours: a gelatinous light-colored precipitate separated in the experiment with 25 mg. of Be.—The experiment was repeated with mixtures of 1 mg. of U as $UO_2(NO_3)_2$ with 5, 10, 15, and 20 mg. of Be: a dark-red color appeared at once in the experiments with 5 and 10 mg. of Be, and on standing dark-red precipitates settled out. In the experiments with 15 and 20 mg. the color was somewhat obscured owing to the presence of iron.—The experiment with 20 mg. of Be and 1 mg. of U was repeated, except that the iron was first removed from the beryllium solution by treatment with Na_2O_2: a good test for uranium was obtained. (From N–B–S, 554.)

P. 106, N. 2.—Behavior of Vanadate with Hydrogen Sulfide in Ammoniacal Solution Alone and in Presence of Ammonium Salts.—See N–B–S, 537.

To 100 mg. of V as Na_3VO_4 in 10 cc. were added 1 cc. of 16 n. HNO_3 and 3 cc. of 15 n. NH_4OH, and the mixture was saturated with H_2S: a large brown precipitate formed when the H_2S was first passed in, and remained when the solution was saturated with H_2S. The precipitate was allowed to settle: it was about 1 cc. in volume, and the solution was deep cherry-red in color. The mixture was filtered and the precipitate was washed with water: it was dark-brown, not black.

P. 106, N. 3.—Action of Acid on Thiovanadate Solution.—See C. E., P. 31, N. 2; also N–B–S, 537–8.

A solution containing in 10 cc. 70 mg. of V as Na_3VO_4, 2 mg. of W as Na_2WO_4, 400 mg. of PO_4 Na_2HPO_4, 3 g. of $NaNO_3$, and 3 cc. of 6 n. HNO_3 was neutralized with NH_4OH, an excess of 5 cc. of 15 n. NH_4OH was added, and the solution was saturated with H_2S: on the first addition of H_2S a small dark precipitate separated, which dissolved before the solution was saturated with H_2S. To the deep-red solution finally obtained was added 6 n. HNO_3 to distinct acid reaction and then 0.5 cc. more: a large black precipitate separated. The mix-

ture was heated nearly to boiling and filtered. The filtrate was treated with NH_4OH, and saturated with H_2S, as before: from the color the amount of vanadium in it was estimated to be 10 mg. The large sulfide precipitate was dissolved in HCl and HNO_3, and tested in the same way: it was found to contain the remaining 60 mg. of V.

The solution containing 10 mg. of V (derived from the HNO_3 filtrate) was boiled for several minutes, HCl and HNO_3 were added, the mixture was boiled again until clear, diluted, and treated by P. 107 to remove PO_4 and test for tungsten: 1–2 mg. of W was found and confirmed by the $SnCl_2$ test, but the H_2WO_4 did not separate on evaporation to 8–10 cc., and appeared only when the mixture was heated with HNO_3 and water after having been allowed to solidify (see C. E., P. 107, N. 3).—The solution containing 60 mg. of V (derived from the HNO_3 precipitate) was evaporated with HNO_3 and a little HCl to 5 cc.: there was a small precipitate, but on diluting, filtering it off, and testing it with $SnCl_2$ by P. 36, no test for tungsten was obtained.

P. 106, N. 4.—Color of Thiomolybdate Solution and its Reaction with Acids.—See C. E., P. 31, N. 1, and N. 2.

P. 106, N. 5.—Action of Acid on Thiotungstate in the Presence of Phosphate.—See C. E., P. 31, N. 2.—For the non-precipitation of tungsten when HNO_3 was added to an $(NH_4)_2S$ solution containing about 95 mg. of W and 500 mg. of PO_4 see C. E., P. 107, N. 1.

To a solution containing 100 mg. of W as Na_2WO_4, 600 mg. of PO_4 as Na_2HPO_4, about 3 g. of $NaNO_3$, and 5 cc. of 6 n. $NH_4C_2H_3O_2$ in a volume of about 110 cc. were added 5 cc. of 15 n. NH_4OH, the mixutre was saturated with H_2S, and the colorless solution was poured into 25 cc. of 6 n. H_2SO_4: a dark-orange solution resulted. After 15 minutes this solution was heated to boiling: at about 80° a small black precipitate of WS_3 separated, which was dissolved in HNO_3 and HCl, precipitated as WO_3 by evaporating with HNO_3 and estimated to contain 5 mg. of W.

P. 106, N. 6.—Action of Hydrogen Peroxide on Vanadic and Molybdic Acids.—See N–B–S, 538–9.

P. 106, N. 7.—Precipitation of Ammonium Metavanadate.—Ammoniacal solutions containing various small quantities of vanadium were treated by P. 106: a small but distinct crystalline precipitate of NH_4VO_3 resulted whenever at least 0.3 mg. of V was present; but the test failed with smaller amounts.

P. 107, N. 1.—Behavior of Tungsten in the Presence of Phosphate in the Analysis of the Aluminum Group.—As to the complete precipitation of tungsten with iron in the ammonium acetate treatment, see

C. E., P. 92, N. 3–8.—As to its insolubility in ether in the presence of 6 n. HCl, see C. E., P. 93, N. 2.

A mixture of 100 mg. of W as Na_2WO_4 and 300 mg. of PO_4 as Na_2HPO_4 was treated by P. 95, 101, 102, 104, and 106: there was no precipitate in the NaOH solution (P. 95) and a scarcely appreciable one in the $NaHCO_3$ solution (P. 101) which probably contained no tungsten. On the addition of $Pb(NO_3)_2$ in P. 102 a moderate white precipitate of $Pb_3(PO_4)_2$ formed, which on analysis was found to contain only 2–3 mg. of W; the PbS, precipitated in the cold, contained not more than 1 mg. of W. With Na_2HPO_4 in P. 104 no precipitate resulted. In P. 106 the NH_4OH solution remained colorless when saturated with H_2S; on acidifying with HNO_3 (volume about 100 cc.) and heating the mixture to boiling, there was a small white precipitate of sulfur, which gave no test for tungsten.

P. 107, N. 2.—Separation of Phosphate from Tungsten.—The H_2SO_4 solution from an earlier experiment (C. E., P. 106, N. 5), which contained 95 mg. of W, 600 mg. of PO_4, $NaNO_3$, $NH_4C_2H_3O_2$ and $(NH_4)_2SO_4$, was evaporated to about 60 cc., and made alkaline with NH_4OH; there were added 3 cc. of 15 n. NH_4OH, and 25 cc. of $Mg(NO_3)_2 \cdot NH_4NO_3$ reagent; the mixture was heated to boiling, allowed to cool, and filtered: the filtrate gave no test for phosphate with ammonium molybdate (P. 91), and the precipitate gave no test for tungsten with $SnCl_2$ (P. 40). See also the experiment described in C. E., P. 106, N. 3.

P. 107, N. 3.—Precipitation of Tungstic Acid by Nitric Acid in the Presence of Salts.—To a solution containing 2 mg. of W as Na_2WO_4, 3 g. of $NaNO_3$, 2 g. of NH_4NO_3, 2 g. of $NH_4C_2H_3O_2$, 10 cc. of 1 n. $Mg(NO_3)_2$ and 5 cc. of 6 n. NH_4OH in a volume of 100 cc., were added 8 cc. of 6 n. HNO_3, and the mixture was boiled; 5 cc. more of 16 n. HNO_3 were added: the solution remained clear.—The experiment was repeated at a volume of 40 cc.: no precipitate separated.—The experiment was repeated at a volume of 20 cc., an excess of 60 milliequivalents of HNO_3 being present in this volume: a slight precipitate separated on boiling. The mixture was allowed to cool, and again boiled: there was now a distinct, light-yellow precipitate. This was filtered off and tested with $SnCl_2$ by P. 36: a blue precipitate was obtained which corresponded to 1–2 mg. of W.

The experiment was repeated. Starting with a volume of 60 cc., the solution was boiled to expel ammonia, 5 cc. of 16 n. HNO_3 were added, and the solution was evaporated: at 25 cc. a slight precipitate was apparent, which increased in size as the evaporation continued. At 10 cc., when allowed to cool, the mixture became solid. It was

heated, 6 cc. of water and 1 cc. of 16 n. HNO_3 were added: there was a distinct white precipitate, which was proved to contain tungsten by the $SnCl_2$ test (P. 36).

The last experiment was repeated except that 50 mg. of V as Na_3VO_4 were also present: no precipitate appeared during the evaporation to 10 cc., showing that the presence of vanadium hinders the precipitation of tungsten. The solid mass obtained on cooling was heated with 1 cc. of 16 n. HNO_3 and 6 cc. of water: a distinct yellow precipitate remained, which was confirmed to be tungsten by the $SnCl_2$ test.

P. 111, N. 1.—Separation of Aluminum from Zinc and from Beryllium by Ether and Hydrogen Chloride.—See Gooch, *Methods of Chemical Analysis*, 214–7 (1912); Gooch and Havens, *Am. J. Sci.* [4], **2**, 416 (1896), *Z. anorg. Chem.*, **13**, 435 (1897); Havens, *Am. J. Sci.* [4], **4**, 111 (1897), **6**, 45 (1898); *Z. anorg. Chem.*, **16**, 15 (1898), **18**, 147 (1898).

Behavior of Beryllium, Uranium, Chromium, and Titanium in the Hydrochloric Acid Ether Process.—See N–B–S, 553, except as to titanium.—10 mg. of Ti as chloride were treated by P. 111: no precipitate separated.

P. 112, N. 1.—Ignition Test for Aluminum with Cobalt.—See N–B–S, 544–5, as to this test, and the effect of the presence of other elements.—For the adsorption of cobalt by $Al(OH)_3$, when precipitated by NH_4OH, see C. E., D. 96.

P. 113, N. 1.—Precipitation of Zinc with Beryllium by Ammonium Hydroxide.—Two mixtures were prepared which contained 50 mg. of Be as nitrate and exactly 20 mg. of Zn, and 2 mg. of Zn, as nitrate; the amounts of zinc being controlled by measuring out the required volumes of stock solutions of $Zn(NO_3)_2$, which had just been analyzed by the $K_4Fe(CN)_6$ titration method of Waring, *J. Am. Chem. Soc.*, **26**, 4 (1904). To each mixture 3 cc. of 6 n. HCl were added, and water to make the volume about 25 cc. Each was treated with NH_4OH as in P. 113. The filtrates were analyzed for zinc by the titration method referred to above: the amounts found were 18.5 and 1.8 mg. Zn, showing that 8 to 10% of the zinc had been carried down by the $Be(OH)_2$.—In other qualitative experiments the presence of some zinc in the precipitates was shown by dissolving the precipitates in HCl, repeating the NH_4OH treatment, and testing the filtrate for zinc with H_2S.—See C. E., D. 96, where it is shown that a much larger proportion of the zinc is carried down by the hydroxides of aluminum, titanium, zirconium, and thorium.

P. 114, N. 3.—Ignition Test for Zinc with Cobalt Salt and Sodium Carbonate.—See N–B–S, 546.

Experiments by M. M. Holm

P. 115, N. 1, 2.—Basic Beryllium Acetate.—See Haber and van Oordt, *Z. anorg. Chem.*, **40**, 465 (1904), for the preparation and properties of basic beryllium acetate, its solubility in $CHCl_3$ and insolubility in water, and its use in preparing a pure beryllium salt when the impurities are iron and aluminum salts. For evidence that the formula is $BeO \cdot 3Be(C_2H_3O_2)_2$, see Wirth, *Z. anorg. Chem.*, 87, 7 (1914).

P. 115, N. 1, 2.—Distribution of Beryllium as Basic Acetate between Chloroform and Water or Dilute Acids.—50 mg. of Be as basic beryllium acetate, prepared from $Be(OH)_2$ as in P. 115, were dissolved in 10 cc. of dry $CHCl_3$, and the solution was subjected to successive treatments with 10 cc. of water or nitric acid; and the amount of beryllium extracted estimated from the size of the precipitate produced by NH_4OH. The first treatment was with water, with 1 minute's shaking: 1.5 mg. of Be was removed. The second was with 10 cc. of 1 n. HNO_3, with 5 minutes' shaking: this removed 2.5 mg. of Be. Then 10 cc. of 1 n. HNO_3 were left in contact with the $CHCl_3$ solution for 24 hours without shaking: this removed 5 mg. of Be. Finally the $CHCl_3$ solution was treated as described in P. 115: a large precipitate of $Be(OH)_2$ was obtained which contained about 40 mg. of Be.

The experiment was repeated with 20 mg. of Be in 10 cc. of $CHCl_3$, the solution being shaken vigorously with 20 cc. of water for 10 minutes: the water extract contained only 1.5 mg. of Be.

50 mg. of Be as $Be(OH)_2$ were dissolved in 20 cc. of 1 n. $HC_2H_3O_2$, and the solution was shaken with 20 cc. of $CHCl_3$ for several minutes; the $CHCl_3$ solution was then treated as described in P. 115: a small precipitate of $Be(OH)_2$ resulted, which contained about 1.5 mg. of Be. The contrast between this result and that in the preceding paragraph shows that the $CHCl_3$ solution in P. 115 does not contain ordinary beryllium acetate.

Dissolving of Basic Beryllium Acetate in Dilute Nitric Acid.—Two portions of 20 mg. of Be as the basic acetate, prepared by the evaporation of (1) a $CHCl_3$ solution and (2) a glacial $HC_2H_3O_2$ solution, were boiled with 10 cc. of 1 n. HNO_3: the residue dissolved completely within 2 minutes.

Behavior towards Chloroform of Uranium, Vanadium, Titanium, Aluminum, Zinc, and Iron after Evaporation of their Solutions in Concentrated Acetic Acid.—A series of experiments were made in which the following substances were treated by P. 115: 50 mg. of U as $UO_2(NO_3)_2$; 50 mg. of U as $UO_2NH_4VO_4$; 50 mg. of V as H_3VO_4; 50 mg. of Ti as $TiO(OH)_2$; 20 mg. of Al as $Al(OH)_3$; and 20 mg. of Zn as $Zn(OH)_2$. In each experiment both the water solu-

tion and the $CHCl_3$ solution were analyzed for the element (or elements) involved: in no experiment, except that with zinc, was any of the element found in either solution; with the zinc several milligrams were found in the water, but none in the $CHCl_3$; in the case of the H_3VO_4 experiment, the residue undissolved by $CHCl_3$ contained much quadrivalent vanadium.

As to the behavior of iron in this process, see Haber and Van Oordt.

Detection by the Treatment with Acetic Acid and Chloroform of Beryllium, Alone and in the Presence of Uranium, Vanadium, Aluminum, Zinc, Iron, and Titanium.—2 and 0.5 mg. of Be as $Be(OH)_2$ were treated by P. 115: a white, flocculent precipitate was finally obtained with NH_4OH in each experiment.—In a control test with the reagents, no precipitate resulted.

To a mixture containing 3 mg. of Be, 50 mg. of U, 2 mg. of Al, 2 mg. of Fe, and 20 mg. of Zn, as nitrates, 10 mg. of V as H_3VO_4, 10 mg. of Ti, as $TiOCl_2$, and some HCl, in a volume of about 30 cc., 6 n. NH_4OH was added in moderate excess, and the precipitate was treated by P. 115: the final precipitate of $Be(OH)_2$ was estimated to contain at least 2 mg. of Be.—The experiment was repeated except that no beryllium was added: it gave a satisfactory blank test for beryllium.

A mixture containing 100 mg. of Be, 3 mg. of Al, 20 mg. of Zn, 3 mg. of Ti, and 3 mg. of Fe (but no U) as nitrates or chlorides was treated by P. 113, the first two paragraphs of P. 115 (the residue being washed once with a few cc. of $CHCl_3$), and P. 116 except that 30 cc. of a 5% $NaHCO_3$ solution were used: on the addition of NH_4OH in P. 116 a white precipitate separated corresponding to 5 mg. of Be.

The experiment was repeated with 5 mg. of Be instead of 100 mg.: there was a small precipitate with NH_4OH in P. 116.

The last experiment was repeated, except that 1 mg. of U as $UO_2(NO_3)_2$ was also present: a yellow precipitate formed with NH_4OH which was larger than the corresponding white precipitate obtained in the experiment without uranium.

P. 116, N. 2, 3.—Behavior of Beryllium Heated with Sodium Hydrocarbonate Solutions in Open Vessels.—N-B-S, 549, state that when 100 cc. of $NaHCO_3$ solutions containing beryllium were boiled for 1 minute in open flasks and filtered, the filtrates were found to contain the following amounts of beryllium:

$NaHCO_3$ content	1%	1.5%	2%	5%
Milligrams of Be	0.1–0.3	1–2	2–4	40–50

Solubility of Uranyl Vanadate in Sodium Hydrocarbonate Solution.—A mixture of 40 mg. of U as $UO_2(NO_3)_2$, 10 mg. of V as Na_3VO_4 and 0.5 g. of $NaHCO_3$ in a total volume of 10 cc. was heated

to boiling: there was no precipitate. To this mixture were added 10 mg. of V and 10 mg. of U, the volume being increased by 2 cc.: there was no precipitate on boiling. 10 mg. more of U were added, and the solution (of volume 13 cc.) was heated to boiling: a yellow precipitate separated. There were added 4 cc. of 5% $NaHCO_3$ solution: the precipitate dissolved almost completely when heated for 2 minutes.

Behavior of Titanium and of Iron with Sodium Hydrocarbonate Solution.—In the experiments tabulated below in which the material was "residue, P. 115" freshly precipitated $TiO(OH)_2$ or $Fe(OH)_3$ was treated by the first two paragraphs of P. 115; each residue undissolved by $CHCl_3$ was then heated with $NaHCO_3$ solution as shown in the table, and the mixture was filtered. The filtrate was acidified and treated with H_2O_2, to estimate the amount of titanium in it; or into it was passed H_2S to estimate (from the depth of the brown color) the amount of iron in it. In the experiments in which the material was $TiOCl_2$ or $Fe(NO_3)_3$ the preliminary treatment of P. 115 was omitted.

Milligrams taken	*Material*	*$NaHCO_3$ solution*	*Treatment*	*Milligrams dissolved*
10 Ti	Residue, P. 115	30 cc. of 10%	Heated to boiling	0.5
20	Residue, P. 115	30 cc. of 10%	Boiled 1 minute	1
19	Residue, last expt.	30 cc. of 10%	Boiled 2 minutes	1
18	Residue, last expt.	30 cc. of 10%	Boiled 3 minutes	1
1	Residue, P. 115	30 cc. of 10 %	Boiled 1 minute	0.8
10	$TiOCl_2$	30 cc. of 5%	Heated to boiling	0.1
10	"	30 cc. of 3%	Heated to boiling	0
10	"	30 cc. of 1%	Heated to boiling	0
5 Fe	Residue, P. 115	30 cc. of 10%	Heated to boiling	1.2
2	" "	20 cc. of 10%	Boiled 1 minute	0.8
5	" "	30 cc. of 5%	Heated to boiling	0.3
10	$Fe(NO_3)_3$	" "	" " "	0.3
10	"	30 cc. of 3%	" " "	0.15
5	Residue, P. 115	" "	" " "	0.15
10	$Fe(NO_3)_3$	30 cc. of 1%	" " "	0.03

Several attempts to remove completely the iron from 5 and 10% $NaHCO_3$ solutions by treatment with H_2S and addition of a ferrous salt in small amount, as recommended by N–B–S, 511, 554, were unsuccessful. The filtrate was colorless only when a slight excess of ferrous salt had been added, and colloidal iron sulfide again formed when this colorless filtrate was treated with H_2S.

ANALYSIS OF NICKEL AND ZIRCONIUM GROUPS ISOLATION OF THE RARE-EARTH GROUP

GENERAL DISCUSSION

D. 126.—Separation of Scandium and Zirconium from Titanium by Ammoniacal Peroxide Solution.—See Classen, *Ber. d. chem. Ges.*, **21**, 370 (1888); Walker, *J. Am. Chem. Soc.*, **20**, 513 (1898).

100 mg. of Ti as hydroxide were evaporated just to fuming with 3 cc. of 6 n. H_2SO_4, and the mixture was cooled and diluted with 20 cc. of water: a clear solution resulted. This solution was added gradually from a separating funnel with constant stirring to a mixture of 40 cc. of 3% H_2O_2 and 10 cc. of 6 n. NH_4OH kept at about 12°: a clear solution resulted. The solution was allowed to stand at 12° over night: it still remained clear.

To one half of the H_2O_2 solution of titanium just described 0.5 mg. of Sc as $ScCl_3$ solution was added: a distinct turbidity appeared. Another 0.5 mg. of Sc was added: a further precipitate separated. This was filtered out, well washed, and evaporated with 6 n. H_2SO_4 to fuming: the characteristic precipitate of $Sc_2(SO_4)_3$ separated. H_2O_2 solution was added to the mixture: the color showed the presence of 1.3 mg. of Ti.

To the other half of the H_2O_2 solution of titanium 0.5 mg. of Zr as nitrate solution was added: the mixture became distinctly turbid. Another 0.5 mg. of Zr was added: the turbidity increased. The precipitate was filtered out, dissolved in dilute H_2SO_4, and the solution was treated with Na_2HPO_4: a small precipitate of zirconium phosphate resulted.

0.5 mg. of Sc and 100 mg. of Ti were evaporated to fuming with 6 cc. of 6 n. H_2SO_4, 20 cc. of water were added, and the mixture was slowly added to an ice-cold mixture of 40 cc. of 3% H_2O_2 and 10 cc. of 6 n. NH_4OH: a turbidity appeared at once, and a coagulated precipitate separated after one hour's standing.

The last experiment was repeated replacing the 0.5 mg. of Sc by 1 mg. of Zr: no precipitate separated after three hours' standing.

100 mg. of Sc and 1 mg. of Ti were heated to fuming with 6 cc. of 6 n. H_2SO_4, and the mixture was diluted with 20 cc. of water, and slowly added to an ice-cold mixture of 40 cc. of 3% H_2O_2 and 10 cc. of 6 n. NH_4OH; the mixture was allowed to stand 30 minutes and filtered; and the filtrate was acidified: it was colorless, showing the absence of titanium. It was evaporated with H_2SO_4 and made alkaline with NH_4OH: no precipitate formed showing the complete precipitation of the scandium.

The last experiment was repeated, replacing the 100 mg. of Sc by 100 mg. of Zr: in the filtrate from the H_2O_2 precipitate 0.1–0.2 mg. of Zr and less than 0.1 mg. of Ti were found present.

Precipitation of Titanium by Ammonium Hydroxide from a Hot Solution Containing Hydrogen Peroxide.—To a solution containing 5 mg. of Ti as chloride and 1 cc. of 1 f. H_2O_2 in 20 cc. were added 5 cc. of 6 n. NH_4OH, and the cold mixture was allowed to stand: the solution remained clear for at least one hour, but there was a precipitate in 1½ hours.—The experiment was repeated, except that the mixture was heated to boiling: a precipitate separated. This was filtered off, and the filtrate acidified; half was tested for titanium with H_2O_2, and half for H_2O_2 with $TiOSO_4$ solution: no color resulted in either test.

The last experiment was repeated with 1 mg. and with 2 mg. of Ti (instead of 5 mg.): no precipitate separated, even when the solution was boiled for 5 minutes. To the hot solutions were added 10 cc. of 3 n. NH_4Cl and 5 cc. of saturated NaCl, respectively: precipitates separated at once, thus showing that the solutions which remained clear after being heated contained colloidal $TiO(OH)_2$.

D. 127.—Separation of the Rare-Earth Elements from Other Elements by Oxalic Acid.—The following experiments were made with oxalic acid to determine the relative advantages of separating the rare-earth elements from those of the aluminum and nickel groups by this reagent and by hydrofluoric acid. (For corresponding experiments with the latter acid, see C. E., P. 131, Note 3.)

To 100 mg. of Th as dry nitrate, 100 mg. of Ce as dry sulfate, and 100 mg. of Y as dry chloride, in separate experiments, were added 50 cc. of nearly saturated oxalic acid solution (containing 10% $H_2C_2O_4 \cdot 2H_2O$); the mixture was boiled for 3 minutes, let stand 10 minutes, and filtered. The filtrate was allowed to stand over night, and was again filtered; and this second filtrate was evaporated with H_2SO_4 to fuming, diluted, and made alkaline with NH_4OH: it was estimated that in the $H_2C_2O_4$ precipitates that formed on standing over night there were 0.0 mg. of Th, 0.2 mg. of Ce, and 0.3 mg. of Y; and that in the filtrates from those precipitates there were 1 mg. of Th, 0.2 mg. of Ce, and 0.3 mg. of Y.

To 500 mg. of Al, 500 mg. of Fe, and 500 mg. of Cr, as dry chlorides, in separate experiments, 50 cc. of 10% $H_2C_2O_4 \cdot 2H_2O$ solution were added, and the mixture was stirred in the cold for 5 minutes; there was no residue or precipitate. The mixture was heated to boiling: there was still no precipitate.

To 100 mg. of Zr as dry $Zr(NO_3)_4$ 50 cc. of 10% $H_2C_2O_4 \cdot 2H_2O$

solution were added, and the mixture was stirred in the cold for two minutes: a clear solution resulted. This was heated to boiling: a slight turbidity appeared. (This was probably due to impurity, as it did not dissolve on adding 10 cc. more of $H_2C_2O_4$ solution.)

To 100 mg. of Ti in the form obtained by evaporating to complete dryness a HCl solution of TiO_2 50 cc. of 10% $H_2C_2O_4 \cdot 2H_2O$ solution were added, and the mixture was stirred in the cold for 5 minutes: there was a fairly large residue. The mixture was boiled for 10 minutes: a small residue remained. It was boiled 5 minutes more: only a few white particles remained.

To 500 mg. of Zn as dry $Zn(NO_3)_2$, 500 mg. of Mn as dry $MnCl_2$, 500 mg. of Ni as dry $NiCl_2$, 500 mg. of Co as dry $CoCl_2$, and 500 mg. of Mg as dry $MgCl_2$ in separate experiments 50 cc. of 10% $H_2C_2O_4 \cdot 2H_2O$ solution were added, and the mixture was stirred in the cold: a large precipitate formed in each case. The solution was boiled for 2 minutes: a large precipitate still remained. The mixture was cooled, allowed to stand for 10 minutes, and then filtered; and the filtrate was evaporated to fuming with H_2SO_4, diluted, and tested for the respective elements (by adding NH_4OH and H_2S in the cases of zinc and manganese, NaOH in the cases of nickel and cobalt, and NH_4OH and Na_2HPO_4 in the case of magnesium): it was estimated that there passed into the filtrate 8 mg. of Zn, 140 mg. of Mn, 2 mg. of Ni, 6 mg. of Co, and 430 mg. of Mg.

To 100 mg. of Sc as dry $ScCl_3$ were added 50 cc. of 10% $H_2C_2O_4 \cdot 2H_2O$ solution, the mixture was boiled for 2 minutes, allowed to stand for 15 minutes, and filtered; and the precipitate was ignited and weighed as Sc_2O_3: 76 mg. of Sc were found to have remained undissolved by the $H_2C_2O_4$ solution and 24 mg. to have passed into solution.

NICKEL GROUP

P. 121, N. 4.—Separation of Manganese from Nickel, Zinc, Iron, Chromium, Aluminum, Uranium, and Thallium, and the Co-Precipitation of Vanadium, Titanium, Zirconium, and Iron.—See N–B–S, 555–6 and 522.

P. 121, N. 4.—Delicacy of Chloric Acid Test for Manganese.—To 1 mg. of Mn as $Mn(NO_3)_2$ and 10 cc. of 16 n. HNO_3 in a small flask in boiling water was added slowly 0.5 cc. of powdered $KClO_3$: a black precipitate separated at once, which was similar in size to that obtained in earlier experiments by boiling the mixture in a casserole. By the latter method 0.1 mg. of Mn could be detected.

To 1 mg. of Mn as $Mn(SO_4)_2$ in 2 cc. of concentrated H_2SO_4 were added 5 cc. of 16 n. HNO_3, the mixture was heated in a casserole over a small flame, and 0.5 cc. of $KClO_3$ was added slowly: there was at first a distinct turbidity, but on boiling for less than 1 minute a clear purple solution resulted, indicating that manganese was present in the solution. The addition of more $KClO_3$ had no effect.

P. 123, N. 2, 3.—Precipitation of Cobalt, Nickel, and Zinc by Hydrogen Sulfide from Acetate Solutions.—See C. E., D. 97.

To a mixture of 250 mg. of Co and 250 mg. of Ni as nitrates 5 cc. of 16 n. HNO_3 were added, and the solution was treated by the first and third paragraphs of P. 123. On the addition of 3 cc. of 6 n. $HC_2H_3O_2$ the solution was clear and reacted acid to litmus. A heavy black precipitate formed at once with H_2S at 70–80°. After the mixture had been treated with H_2S for 1 minute, allowed to stand for 5 minutes, and shaken, there was still a strong odor of H_2S. The mixture was treated again with H_2S, and filtered; the filtrate was made alkaline with NH_4OH, and H_2S was added: the solution remained colorless, showing that the precipitation of cobalt and nickel as sulfides had been complete in the acid solution.

The experiment was repeated with a mixture of 2 mg. of Co, 2 mg. of Ni, and 100 mg. of Zn as nitrates: in the treatment with H_2S at 70–80° a white precipitate formed at once and began to darken after 30 seconds; the dark color continued to increase during the 5 minutes' standing, but not in the second treatment with H_2S; the filtrate contained no cobalt, nickel, or zinc.

The last experiment was repeated with 5 mg. of Co, 5 mg. of Ni, and 100 mg. of Zn: the results were the same.

P. 123, N. 2–4.—Separation of Cobalt, Nickel, and Zinc from Cerium and Thorium by Hydrogen Sulfide in Acetate Solutions.—To a mixture of 150 mg. of Ce, 2 mg. of Co, and 2 mg. of Ni as nitrates were added 5 cc. of 16 n. HNO_3, and the solution was treated by P.

123: when the 3 cc. of 6 n. $HC_2H_3O_2$ were added there remained in the acid solution a very slight turbidity, which persisted but did not increase when the 10 cc. of 3 n. $NH_4C_2H_3O_2$ were added and the mixture was heated to 70–80°. The black H_2S precipitate was heated with HCl and HNO_3, the mixture was filtered, and the filtrate was made alkaline with NH_4OH: there was no precipitate, showing that no cerium was precipitated with the CoS and NiS.

The experiment was repeated with 120 mg. of Th as nitrate: the solution became slightly turbid when the acid-acetate solution was heated to 70–80° and there was a distinct, white, suspended precipitate after the first H_2S treatment. The precipitate was collected on a filter without difficulty, washed, dissolved in HCl, and the solution was made alkaline with NH_4OH: a small white precipitate separated, which was estimated to contain less than 1 mg. of Th. The clear filtrate containing nearly all the thorium became slightly turbid within 15 minutes. The mixture was heated at 70–80° for 1 minute and allowed to stand for 5 minutes: the turbidity increased gradually. The mixture was boiled for 3 minutes, and allowed to stand for 12 hours: the precipitate, which had settled, was estimated to contain about 7 mg. of Th. While a small quantity of thorium (when much is present) may separate with the cobalt, nickel, and zinc, the precipitation of thorium is slow at 70–80°, and is not rapid even at 100°.

P. 123, N. 4.—Insolubility of Titanium and Zirconium Hydroxides in Acetic Acid and Ammonium Acetate.—See C. E., P. 92, N. 3–8.

To 2 mg. of Ti as $TiO(OH)_2$ in HCl were added 5 cc. of 16 n. HNO_3, and the solution was treated by the first and third paragraphs of P. 123: the white NH_4OH precipitate did not dissolve when the 3 cc. of 6 n. $HC_2H_3O_2$ were added, although the solution was acid. After the addition of the 10 cc. of 3 n. $NH_4C_2H_3O_2$ the mixture was filtered, and the filtrate was tested for titanium with H_2O_2: no color appeared, showing that no $TiO(OH)_2$ had dissolved.

The experiment was repeated with 10 mg. of Zr as $ZrO(OH)_2$ in HCl, and the filtrate was made alkaline with NH_4OH and heated: there was no precipitate, showing that no $ZrO(OH)_2$ had dissolved in the acetic acid.

The two experiments were repeated except that the mixtures, after the addition of $NH_4C_2H_3O_2$, were heated to boiling: the filtrates again contained no titanium or zirconium.

P. 124, N. 1, 3.—Allotropic Forms and Solubility Relations of Nickel and Cobalt Sulfides.—Thiel and Gessner, *Z. anorg. Chem.*, **86**, 1–57 (1914), have concluded that there are three allotropic forms of NiS: the *α* form, the most soluble one, which dissolves readily in cold 2 n.

HCl; the β form, which dissolves only to a slight extent in cold 2 n. HCl (about 40 mg. of Ni per liter), but which may be removed by digestion with hot 2 n. HCl; and the γ form, the least soluble one, which remains after this digestion. When solutions of sodium sulfide and a nickel salt are mixed rapidly at room temperature, with exclusion of oxygen, the precipitate first formed consists largely of α NiS. This on standing is transformed into the β form, and to some extent into the γ form. The transformation is favored by higher temperature, exposure to air, and presence of acid or of NH_4OH. As might be expected, the precipitate formed slowly by passing H_2S into a hot acid solution (acetic acid and an acetate) contains a relatively small proportion of the α form. The β and γ forms are crystalline and are suggested to be polymers of the α form.

The corresponding investigation of CoS, planned by Thiel and Gessner, appears not to have been completed. Their preliminary experiments (*l. c.* 55) indicate that the speed of transformation of α CoS into a less soluble form is greater than in the case of nickel. Herz, *Z. anorg. Chem.*, **27**, 390, and **28**, 343 (1901), had already shown that a part of a fresh precipitate of CoS (or NiS) dissolves rapidly in HCl of concentration less than 0.5 n.

Dunn and Rideal, *J. Chem. Soc. London*, **123**, 1242–51 (1923), concluded that the reaction between oxygen and a suspension of β NiS takes place at the surface of the solid sulfide. One set of experiments shows that the rate of the oxygen reaction is less for γ NiS than for β NiS; they state that the rate is much faster in the case of α NiS.

Thiel and Gessner gave one "unexplained" experimental result which throws doubt on their figures for the solubility of β and of γ NiS. These were based on a large number of experiments in which various samples of the β or γ sulfides were shaken with 2 n. HCl saturated with H_2S; a small amount of nickel dissolved rapidly, and the amount seemed not to increase appreciably after half an hour. Thus with β NiS at room temperature 100 cc. of 2 n. HCl dissolved 3.0–5.1 mg. of Ni in ½ hour in 4 experiments, 3.1–4.0 mg. in 15 hours in 3 experiments, and 2.9 mg. in 42 hours in 1 experiment. Nevertheless this "equilibrium state" could not be approached from the other side, by saturating an acid solution of a nickel salt with H_2S in the presence of solid β or γ NiS.

Since the precipitation reaction in acid solution, $Ni^{++} + H_2S \rightleftharpoons NiS$ (β or γ) $+ 2H^+$, has thus been shown to be extremely slow, it seems more probable that the reverse reaction in the neighborhood of the equilibrium is also extremely slow than that it proceeds rapidly to equilibrium (as Thiel and Gessner assumed). Moreover, the experi-

ments of N–B–S (p. 528) on the amounts of NiS that dissolved in successive treatments with 1.1 n. HCl at room temperature in a current of H_2S are not in agreement with the results of T. and G. In the fifth 15-minute treatment (when *a* NiS should no longer be present), 10 mg. of Ni dissolved in 30 cc.; which is about 8 times the quantity per unit volume found by T. and G. Also in the last treatment, of 6 hours' duration, 25 or 30 mg. of Ni dissolved in 30 cc. and the undissolved remainder contained only about 30 mg. of the 200 mg. of Ni in the original NiS sample. At that time it was concluded that the dissolving of NiS in 1.1 n. acid is a slow but continuous process. Comparison with the results of T. and G. in 2 n. acid suggests that the rate of solution decreases with increasing concentration of acid.

These conclusions receive support from the work of Glixelli, *Z. anorg. Chem.*, **55**, 297–320 (1907), with ZnS; and from the early work of Baubigny, *Compt. rend.*, **94**, **95** (1882), **107**, 751 (1887), with NiS and CoS, discussed by Glixelli. The latter concludes that the phenomena observed with NiS and CoS are not peculiar to these sulfides alone, but are shown also by ZnS, though in a letter degree. In the precipitation of sulfide in acid solution an induction period (before the precipitate can be detected) was observed in the case of ZnS, but was much shorter than that for NiS or CoS; the induction periods increased with increasing concentration of H^+. Also the establishment of the solubility equilibrium for ZnS in acid solution is a slow process, and the rate is slower at higher concentrations of H^+. Glixelli believes that this slowness will be much more marked in the case of NiS or CoS. See also Bruner (*Bull. internat. de l'academie des sciences de Cracovie*, 1906, 603) for a discussion of Glixelli's preliminary results. Padoa and Cambi, *Gazz. chim. ital.*, **37**, II, 111–122 (1907), agree with the conclusions of Bruner and Glixelli with regard to the sulfides of zinc, cobalt, and nickel.

In connection with Glixelli's work on the slowness of the ZnS reaction, an experiment of N–B–S, p. 529, may be cited. A mixture of 500 mg. of Zn and 2 mg. of Ni as sulfides (freshly precipitated by NH_4OH and $(NH_4)_2S$) was shaken with 30 cc. of 1.1 n. HCl at room temperature for 10 minutes: the solution contained only about 100 mg. of Zn. In a second treatment, which continued many hours, about 300 mg. of Zn dissolved.

P. 124, N. 1, 3.—Action of Hydrochloric Acid on Nickel Sulfide when Other Sulfides Are Present.—The experiments of N–B–S, 529, show that small amounts of NiS may sometimes be dissolved completely by 1.1 n. HCl when distributed throughout a large precipitate of FeS, but that they are not readily dissolved out of ZnS or MnS.

ISOLATION OF RARE EARTHS

P. 131, N. 3.—Precipitation of Rare-Earths by Hydrofluoric Acid.—To 1 mg. of Yb as dry $YbCl_3$ 2 cc. of water, 0.5 cc. of 27 n. HF, and 10 cc. of 0.6 n. HCl were added: a turbidity appeared at once. The mixture was heated on a steam-bath: the precipitate coagulated.

Separation of Rare-Earth Elements from Other Elements by Hydrofluoric Acid.—To 100 mg. of Th as dry $Th(NO_3)_4$, 100 mg. of Ce as dry $Ce_2(SO_4)_3$, and 100 mg. of Y as dry YCl_3, in separate experiments, 25 cc. of 48% HF were added; the mixture was heated on a steam-bath for 2 minutes, diluted with 25 cc. of water and again heated for 3 minutes on a steam-bath, cooled, and allowed to stand for 10 minutes: there was a large precipitate in each case. This was filtered out, the filtrate was evaporated to fuming with a few drops of 95% H_2SO_4, diluted, made alkaline with NH_4OH, and allowed to stand: very small precipitates formed which were estimated to consist of 0.4 mg. of Th, 0.1 mg. of Ce, and 0.2 mg. of Y, respectively.

To 100 mg. of Sc as dry $ScCl_3$ were added 25 cc. of 48% HF and 25 cc. of water, the mixture was heated to boiling and filtered; both the precipitate and the filtrate were heated with H_2SO_4 to fuming, the solutions were diluted and made alkaline with NH_4OH, and the precipitates were ignited and weighed: 85 mg. of Sc were found in the residue undissolved by the HF and 15 mg. of Sc in the HF solution.

To 500 mg. of Al as dry $AlCl_3$ and to 500 mg. of Cr as dry green $CrCl_3$ in separate experiments 25 cc. of 48% HF were added: a large precipitate formed. The mixture was heated nearly to boiling and stirred: a large residue still remained. The mixture was diluted with 25 cc. of water and heated: the residue dissolved completely.

To 500 mg. of ferric Fe, Mn, Zn, Ni, and Co, in the form of the dry chlorides, in separate experiments, 5 cc. of 48% HF were added: complete solution resulted in the iron, manganese, and zinc experiments, but there was a small residue in the nickel and cobalt experiments. To each mixture 5 cc. more HF solution were added: the nickel and cobalt residues dissolved completely. The mixtures were heated to boiling: all the solutions remained clear, except that of manganese from which there separated a considerable slimy pink precipitate, which remained after standing in the cold and on adding 15 cc. more of HF solution. Each mixture was diluted with an equal volume of water and heated on a steam-bath for 3 minutes: the manganese mixture became clear, and the other solutions remained so.

To 100 mg. of Zr as dry $ZrCl_4$, 100 mg. of Ti as dry TiO_2, 100 mg. of U as dry $UO_2(NO_3)_2$, 100 mg. of Be as dry $BeCl_2$, 100 mg. of V

as dry $VOCl_2$, and 100 mg. of V as dry Na_3VO_3, in separate experiments, 10 cc. of 48% HF were added: in each case a clear solution resulted. The solution was heated to boiling: in each case the solution remained clear. An equal volume of water was added, and the solution was heated on a steam-bath for 3 minutes: the solutions were still clear.

To 500 mg. of Mg as dry $MgCl_2$ 25 cc. of 48% HF were added: a large precipitate separated. The mixture was diluted with 25 cc. of water, heated on a steam-bath for 3 minutes, allowed to stand 10 minutes, and filtered; the filtrate was evaporated to fuming with H_2SO_4, diluted to 50 cc., neutralized with NH_4OH, treated with 15 cc. of 15 n. NH_4OH and 50 cc. of 10% $Na_2HPO_4 \cdot 12H_2O$ solution, and allowed to stand over night: a small precipitate formed which was estimated to contain 1 mg. of Mg.

P. 131, N. 4.—Effect of Hydrochloric Acid on the Precipitation of Scandium as Fluoride.—To 1 mg. of Sc as $ScCl_3$ in 2 cc. of water were added ½ cc. of 27 n. HF and 10 cc. of HCl of the strength shown in the table below. The resulting mixture, which was almost always clear, was heated for 4–5 minutes on a steam-bath, the time being counted from the instant when the vessel was placed on the bath. The mixture was poured into a pyrex flask, observed at once, and then cooled under the tap, and further observations made after standing (no etching being noticed with the concentration of HF used). In Expts. 6, 7, and 8, after on hour 1 g. of NH_4Cl was added: coagulation then became more rapid. In Expt. 4, which was tried twice, the order in which the two acids were mixed was reversed, the HCl being added first.

Expt. No.	*Normality of added HCl*	*Effect after heating*	*Effect after standing*
1	0.0	None	None.
2	0.15	Slight turbidity	Not coagulated after 2 hours.
3	0.3	Turbidity	———
4	0.3	None	———
5	0.6	Turbidity	Slight coagulation after 1 hour.
6	0.8	Turbidity	Began to settle in 1 hour.
7	1.0	Turbidity	Began to settle in 1 hour.
8	1.2	Turbidity	Began to settle in 1 hour.
9	1.5	Turbidity	Began to settle in 40 minutes.
10	2	Turbidity	Began to settle in 30 minutes.
11	3	None	Slight turbidity in 15 minutes; no more after 2 hours.

10 mg. of Sc in 2 cc. of water were heated with 0.5 cc. of 27 n. HF and 10 cc. of 0.6 n. HCl on a steam-bath for 4–5 minutes, and filtered: the precipitate ran through the filter. 1 g. of NH_4Cl was added: this

coagulated the precipitate. The mixture was filtered. The filtrate was evaporated to fuming after adding a few drops of 6 n. H_2SO_4; the residue was dissolved in water, and NH_4OH was added: no precipitate could be observed, showing that the filtrate contained no scandium.—This experiment was repeated with 2 mg. of Sc and 100 mg. of Ti, except that no NH_4Cl was added. The small precipitate, which coagulated fairly rapidly, was collected on a filter; 5 cc. of hot 6 n. HCl were poured through the filter twice; the extract, in a platinum dish, was fumed with a few drops of 6 n. H_2SO_4, the residue taken up in 10 cc. of water and 1 cc. of 6 n. HCl, and 1 cc. of 3% H_2O_2 added: there was a barely perceptible coloration, showing that scarcely any titanium was present. NH_4OH in excess was then added: a white gelatinous precipitate resulted, whose size was about that produced by 2 mg. of Sc.

P. 131, N. 5.—Separation of Zirconium and Titanium from Rare-Earth Elements by a Small Volume of Hydrofluoric Acid.—100 mg. of Zr as $Zr(NO_3)_4$ were evaporated just to dryness with HCl, and to the residue 0.5 cc. of 48% HF were added: a pasty residue resulted. 10 cc. of water were added: a clear solution resulted.

100 mg. of Ti as $TiOCl_2$ were evaporated just to dryness with HCl, and to the residue 0.5 cc. of 48% HF were added, and the mixture was gently warmed: a clear solution resulted.

To a mixture of 100 mg. of Ce, 1½ mg. of Sc, 1 mg. of Zr, and 1 mg. of Ti as dry chlorides 0.5 cc. of 48% HF was added, the mixture was heated for 1 minute, diluted with 10 cc. of water, and filtered; the filtrate was evaporated with 1 cc. of 6 n. H_2SO_4 and treated with 5 cc. of water, 10 cc. of 3% H_2O_2, and 10 cc. of 10% $Na_2HPO_4 \cdot 10H_2O$: a precipitate formed corresponding to 0.2 mg. of Zr and a color corresponding to 1 mg. of Ti. The mixture was filtered, and to the filtrate Na_2SO_3 was added: a precipitate formed corresponding to about 2 mg. of Ti (probably owing to the presence of some zirconium).

P. 131, N. 5.—Behavior of Indium with Hydrofluoric Acid, Alone and in Presence of Cerium.—100 mg. of In as $InCl_3$ in 0.1 n. HCl were evaporated to dryness on a steam-bath, and 0.5 cc. of 27 n. HF was added: the residue all dissolved. 2 cc. of water and then 8 cc. of water were added: the solution remained clear.

Solutions containing 100 mg. of Ce as $Ce(NO_3)_3$ with 1 mg. of In as $InCl_3$ in one experiment and with 5 mg. of In in another experiment were evaporated to dryness on the steam-bath; 2 cc. of water and then 0.5 cc. of 27 n. HF were added, and the mixtures were warmed on a steam-bath with occasionally stirring for 3 minutes; the solutions were filtered, the filtrates made neutral to litmus with 6 n. NH_4OH, 0.05 cc.

of 27 n. HF added, and the filtrates saturated with H_2S: the filtrate from the solution with 1 mg. of In gave a barely perceptible precipitate. This was dissolved and reprecipitated by H_2S from 6 n. $HC_2H_3O_2$: it gave a precipitate corresponding to 0.3 mg. of In; the filtrate from the solution with 5 mg. of In gave a precipitate which when reprecipitated from 6 n. $HC_2H_3O_2$ corresponded to 0.5–1.0 mg. of In

To 100 mg. of Ce as $Ce(NO_3)_3$ in 5 cc. of water at 50° 0.5 cc. of 27 n. HF was added with stirring: a large white flocculent precipitate resulted. 5 cc. of solution containing 5 mg. of In as $InCl_3$ were added slowly, and the mixture was kept warm for 3 minutes, then cooled, and filtered; the filtrate was made neutral to litmus with 6 n. NH_4OH, 0.05 cc. of 27 n. HF were added, and the solution was saturated with H_2S: a yellow precipitate separated out after 30 minutes. This was reprecipitated from 6 n. $HC_2H_3O_2$ by H_2S: it gave a precipitate corresponding to only 1 mg. of In.

ZIRCONIUM GROUP

P. 132, N. 1, 2.—Precipitation of Elements from Fluoride Solutions by Hydrogen Sulfide.—To solutions containing in a volume of 10 cc. the number of milligrams of the elements shown in the first column 0.5 cc. of 27 n. HF was added, and the mixture was made neutral to litmus with 6 n. NH_4OH; then the volume of 27 n. HF shown in the second column was added, the cold solution was saturated with H_2S, and allowed to stand. The results are shown in the last column.

Milligrams taken	*Cc. of HF added*	*Result with H_2S*	
		Within 5 minutes	*After 25 minutes*
2 In	0.05	Small suspended ppt.	—
2 In	0.20	No ppt.	No ppt.
1 In	0.05	Slight turbidity	—
1 In	0.12	Slight turbidity	—
1 In 30 Ti	0.10	Yellow ppt.[a]	—
1 In 100 Zr	0.05	Yellow ppt.	—
1 In 10 Fe^{II}	0.05	Yellow ppt.	—
30 Ni	0.10	Small black ppt.	0.5 mg. ppted.
50 Ni	0.05	Small black ppt.	1.5 mg. ppted.
30 Co	0.05	Small black ppt.	1 mg. ppted.
30 Zn	0.1	Large white ppt.	—
0.5 Zn	0.1	White ppt.	—
0.5 Zn	0.5	White ppt.	—
10 Fe^{II}	0.05	No ppt.	No ppt.

[a] Indium was confirmed by reprecipitating from 6 n. $HC_2H_3O_2$.

A mixture of 1 mg. of In as $InCl_3$ and 10 mg. of Ni as $Ni(NO_3)_2$ was treated as described above: a black precipitate appeared almost immediately, and gradually increased in size. After 15 minutes it was collected on a filter; it was estimated to contain 2–3 mg. of Ni. A cold 5-cc. portion of 6 n. HCl was poured 3 times through the filter (without dissolving much NiS), the solution was boiled, and treated with 6 n. NH_4OH, an excess of 2 cc. being added: a very small white precipitate formed. This was filtered, dissolved in 10 cc. of 6 n. $HC_2H_3O_2$, and the solution saturated with H_2S: a small yellow precipitate formed which was estimated to correspond to 0.3 mg. of In.— The experiment was repeated, except that the Ni was replaced by Co, and the fluoride-H_2S mixture allowed to stand 20 minutes before filtering: the black sulfide precipitate was estimated to contain 6–8 mg. of

Co. In the test with H_2S in $HC_2H_3O_2$ solution, a yellow precipitate corresponding to ½ mg. of In was obtained.

P. 132, N. 1–3.—Precipitation of Indium by Hydrogen Sulfide from Fluoride Solution.—A solution containing in 10 cc. of water 100 mg. of In, 0.5 cc. of 27 n. HF exactly neutralized with 6 n. NH_4OH, and 0.05 cc. of free 27 n. HF was saturated with H_2S: a large yellowish-white precipitate separated. This was filtered out after standing 10 minutes, and the filtrate was resaturated with H_2S: a yellowish-white precipitate again separated. The mixture was filtered, and the filtrate resaturated with H_2S three times more: it yielded a precipitate each time. The clear solution resulting from this treatment was boiled to expel the H_2S, was made neutral to litmus, 0.05 cc. of 27 n. HF was added, and the mixture saturated with H_2S: a pale-yellow precipitate separated, which was shown to contain 0.7 mg. of In by reprecipitating from 6 n. $HC_2H_3O_2$ solution.

In two separate experiments 1 mg. and 2 mg. of In as $InCl_3$ were added to NH_4F solutions obtained by making 5-cc. portions of 27 n. HF as nearly neutral as possible to litmus with 15 n. NH_4OH; and these solutions were then saturated with H_2S: the one with 1 mg. of In gave only a barely recognizable precipitate after 3 hours; but that with 2 mg. gave a well coagulated precipitate after one hour.

P. 133, N. 1.—Precipitation of Indium Sulfide from Acetic Acid Solutions.—Wada and Ato, *Sci. Papers Inst. Phys. Chem. Research*, 1, 68, 76 (1922), developed the method of testing for indium used in P. 133, and showed that less than 0.5 mg. of In can be detected by H_2S in 10 cc. of 6 n. $HC_2H_3O_2$.

In three separate experiments a 10-cc. portion of 6 n. $HC_2H_3O_2$ containing 0.5, 1, and 2 mg. of In as $InCl_3$, at 50–60° was saturated with H_2S: 0.5 mg. of In gave a pale-yellow precipitate immediately, which coagulated and became deeper yellow within 3 minutes; the other two gave light-yellow precipitates which coagulated immediately; after settling, the size of the precipitate in the 0.5-mg. experiment was 1/4 or 1/3 of that in the 1 mg. experiment.

P. 133, N. 2.—Behavior of Zinc, Nickel, Cobalt, Iron, and Zirconium with Hydrogen Sulfide in Six Normal Acetic Acid.—In separate experiments, 20, 3, and 0.5 mg. of Zn as $Zn(NO_3)_2$ were dissolved in 10 cc. of 6 n. $HC_2H_3O_2$ and the solution was saturated with H_2S: in each case a white precipitate formed immediately.

5 mg. of Ni as $Ni(NO_3)_2$ were added to 10 cc. of 6 n. $HC_2H_3O_2$, and the solution at 50–60° was saturated with H_2S: there was no precipitate, even on standing over night.—The experiment was repeated with 5 mg. of Co, with the same result.

500 mg. of Ni as $Ni(NO_3)_2$ were dissolved in 10 cc. of 6 n. $HC_2H_3O_2$, and the cold solution was saturated with H_2S: a small black precipitate slowly separated. After half an hour the mixture was filtered, and the filtrate saturated with H_2S: there was no precipitate in 10 minutes. 0.25 cc. of 3 n. $NH_4C_2H_3O_2$ were slowly added with shaking: there was a slight turbidity in 15 minutes, and a large black precipitate settled out on standing over night.—The experiment was repeated with 500 mg. of Co as $Co(NO_3)_2$: the results were similar, except that less sulfide precipitated on standing over night.

10 cc. of 6 n. $HC_2H_3O_2$ containing 1 mg. of Fe as $Fe(NO_3)_3$ were saturated with H_2S at room temperature: the solution became turbid due to the formation of finely divided sulfur, and the reaction seemed to be complete within about 10 minutes.

An HCl solution containing 100 mg. of Zr as chloride was evaporated just to dryness on a steam-bath, cooled, and treated with 10 cc. of 6 n. $HC_2H_3O_2$: complete solution resulted, and after half an hour the solution was clear except for a slight opalescence. It was then saturated with H_2S: there was no change. It was filtered, again saturated with H_2S, and allowed to stand over night: no precipitate separated.

Behavior of Titanium Chloride with Cold 6-Normal Acetic Acid.—An HCl solution containing 30 mg. of Ti as chloride was evaporated to dryness on a steam-bath; the residue, after being heated on the bath for 20 minutes, was cooled, and treated with 10 cc. of 6 n. $HC_2H_3O_2$: the $TiOCl_2$ dissolved, but a white precipitate appeared almost at once, and rapidly increased in size.

P. 134. N. 3.—Behavior of Cobalt, Uranium, Thorium, Scandium, and Indium in the Phosphate Precipitations.—See N–B–S, 560, as to cobalt, uranium, and thorium.

30 mg. of Sc were evaporated to fuming with 2 cc. of 6 n. H_2SO_4, and to the cooled mixture were added 5 cc. of water, 10 cc. of 3% H_2O_2 solution, and 10 cc. of 0.9 n. Na_2HPO_4 solution: no precipitate formed even after three hours' standing.

100 mg. of Ti, and a mixture of 100 mg. of Ti and 1 mg. of Sc, were evaporated to fuming with 4 cc. of 6 n. H_2SO_4; 15 cc. of water, 25 cc. of 3% H_2O_2 solution, and 20 cc. of 0.9 n. Na_2HPO_4 solution were added, and the mixtures were allowed to stand one hour: no precipitate formed in either solution. The solutions were boiled in contact with platinum foil for 50 minutes, replacing the water that evaporated: a large precipitate separated, but the liquid was still yellow. 1.5 g. of solid $Na_2SO_3 \cdot 7H_2O$ were added, and after standing an hour the mixtures were filtered, and 6 n. NH_4OH was added to the

filtrates: a small precipitate formed in each solution. These precipitates were dissolved in HCl, the solutions evaporated to dryness, 8 drops of 48% HF and 8 drops of 6 n. NH_4OH were added: there was a very small residue in each case. The mixtures were filtered, the filtrates evaporated to fuming with H_2SO_4, and diluted and made alkaline with NH_4OH: no precipitate formed in either case, showing that neither titanium nor scandium passed into the filtrate from the Na_2SO_3 precipitate.

A mixture of 100 mg. of Ti and 5 mg. of Sc was evaporated with 4 cc. of 6 n. H_2SO_4; 15 cc. of water, 25 cc. of 3% H_2O_2 solution, and 20 cc. of 0.9 n. Na_2HPO_4 solution were added: no precipitate formed. The solution was boiled for 20 minutes, 3 g. of dry $Na_2SO_3 \cdot 7H_2O$ were added, and after 30 minutes the precipitate was filtered out, and NH_4OH was added to the filtrate: no precipitate resulted, showing that the scandium was all precipitated with the titanium.

Wada and Ato, *Sci. Papers Inst. Phys. Chem. Research,* **1**, 71–72 (1922), have described the following experiments with indium. Each mixture was evaporated to fuming with 1 cc. of 6.7 n. H_2SO_4; then 5 cc. of water, 10 cc. of 3% H_2O_2, and 10 cc. of 0.9 n. Na_2HPO_4 were added, and the mixture let stand an hour; any precipitate was filtered off, powdered $NaHSO_3$ gradually added to the hot filtrate till it was decolorized, and the mixture filtered after half an hour; the filtrate was then made slightly alkaline with NH_4OH. The precipitate, which always contained some titanium when this element was present, was tested for indium. The results, expressed in milligrams, are as follows.

Mixture analyzed			*Indium found*
Zr	*Ti*	*In*	
2	2	2	2
—	10	1	1
—	50	2	Trace
50	—	2	Trace
50	50	2	0

The separation of indium from zirconium and titanium recommended by Wada and Ato is the precipitation of In_2S_3 by $(NH_4)_2S$ from a neutral solution containing tartrate.

ANALYSIS OF THE RARE-EARTH GROUP

EXPERIMENTS MAINLY BY ISOBURO WADA

D. 141.—Separation of Scandium from Rare-Earth Elements and Zinc by Acid Ammonium Oxalate.—10 mg. of Sc as dry $ScCl_3$ were heated with 30 cc. of 5% $(NH_4)_2C_2O_4 \cdot H_2O$ solution and 3 cc. of 10% $H_2C_2O_4 \cdot 2H_2O$ solution: a clear solution resulted. The solution was cooled: a small crystalline precipitate formed. 50 cc. of cold water were added: some of the precipitate was still undissolved. The mixture was filtered; the residue and solution were separately heated to fuming with H_2SO_4, and water and NH_4OH were added: the residue gave a precipitate corresponding to 0.8 mg. of Sc, and the solution gave one corresponding to about 9 mg. of Sc.

100 mg. of Th as precipitated $Th(C_2O_4)_2$ were treated in the cold with 50 cc. of 5% $(NH_4)_2C_2O_4 \cdot H_2O$ and 5 cc. of 10% $H_2C_2O_4 \cdot 2H_2O$ solution: a large part of the precipitate dissolved. The mixture was then heated to 60°: the precipitate dissolved completely.

100 mg. of Ce and 100 mg. of Y as precipitated oxalates in separate experiments were boiled for 5 minutes with 50 cc. of 5% $(NH_4)_2C_2O_4 \cdot H_2O$ and 5 cc. of 10% $H_2C_2O_4 \cdot 2H_2O$ solution, the mixtures were cooled, allowed to stand 10 minutes, and filtered; the filtrates were evaporated to fuming with H_2SO_4, diluted, and made alkaline with NH_4OH: the NH_4OH precipitates were estimated to contain 1.2 mg. of Ce and 10 mg. of Y respectively.

500 mg. of Zn as precipitated ZnC_2O_4 were treated as in the last experiment, except that H_2S was passed into the NH_4OH solution at the end: the H_2S precipitate was estimated to contain 230 mg. of Zn.

D. 145.—Behavior of Rare-Earth Elements towards Concentrated Formic Acid.—To 1 mg., 1.5 mg., and 2 mg. of Sm as dry nitrate in separate test-tubes 5 cc. of 95% $HCHO_2$ were added: clear solutions resulted. These were boiled for just one minute: a precipitate separated from each solution. The mixture containing 1 mg. of Sm was filtered, the precipitate was dissolved in HNO_3, and the filtrate was evaporated with HNO_3; NH_4OH was added to each, and the precipitates were compared: only about 0.25 mg. of Sm failed to be precipitated by the $HCHO_2$.

100 mg. of Pr and 100 mg. of Nd as dry chlorides were separately treated as just described: a turbid mixture resulted in the cold, and a large precipitate separated suddenly upon boiling. The mixtures were allowed to stand for an hour: the supernatant liquids were green and pink respectively, showing incomplete precipitation (possibly owing to the HCl coming from the metathesis).

To 100 mg. of La, 100 mg. of Pr, and 100 mg. of Nd as dry chlo-

rides in separate testtubes 10 cc. of 95% $HCHO_2$ were added: clear solutions resulted. The solutions were boiled: a large precipitate suddenly separated from the neodymium mixture after boiling 60 seconds; and from the praseodymium mixture after boiling 90 seconds; but none separated from the lanthanum solution even after 120 seconds. To the lanthanum solution 2 mg. of Sm in $HCHO_2$ solution were added, and the solution was heated to boiling: a large precipitate suddenly separated, attended by violent bumping.

P. 141, N. 1.—Behavior of Scandium and Rare-Earth Elements towards Acid Ammonium Fluoride.—100 mg. of Sc as dry $ScCl_3$ were treated in the cold with 10 cc. of a mixture of two volumes of 48% HF and one volume of 15 n. NH_4OH: a considerable precipitate separated. 5 cc. more of the mixture were added: most of the precipitate dissolved. The mixture was warmed slightly: the rest of the precipitate dissolved. The mixture was cooled to room-temperature: a small crystalline precipitate separated. 8 cc. of water were added: the precipitate redissolved.

In separate experiments 100 mg. of Th, 100 mg. of Ce, and 100 mg. of Y, as dry chlorides, were heated for 10 minutes on a steam-bath with a mixture of 10 cc. of 48% HF and 13 cc. of 6 n. NH_4OH; the mixture was then filtered, the filtrate evaporated with H_2SO_4, cooled, diluted, and made alkaline with NH_4OH: no precipitate separated in any of the three filtrates.

The preceding experiments were repeated with mixtures of 100 mg. of Th and 1 mg. of Sc, 100 mg. of Ce and 1 mg. of Sc, and 100 mg. of Y and 1 mg. of Sc: in every case a precipitate (of $Sc(OH)_3$) was obtained from the filtrate from the fluoride precipitate.

To a mixture of 100 mg. of Ce, 1½ mg. of Sc, 1 mg. of Zr, and 1 mg. of Ti as dry chlorides 0.5 cc. of 48% HF was added, the mixture was heated for a minute on a steam-bath, diluted with 10 cc. of water, and filtered; the precipitate was heated on a steam-bath with frequent stirring for 2 minutes with 5 cc. of 48% HF and 10 cc. of 6 n. NH_4OH, and filtered; and the filtrate was evaporated to dryness, and the residue was heated to strong fuming with 1 cc. of 95% H_2SO_4: a small white precipitate estimated to correspond to 0.6 mg. of Sc separated (showing that this amount of scandium was extracted from the fluoride precipitate). This mixture was diluted with 10 cc. of water, made alkaline with NH_4OH, and filtered; the precipitate was dissolved in HCl, the solution was evaporated, and the residue was treated with 5 drops of water and 10 drops of 48% HF: a faint turbidity appeared, and on short standing a very small flocculent precipitate separated (confirming the extraction of the scandium).

P. 141, N. 1.—Behavior of Cobalt and Nickel towards Acid Ammonium Fluoride.—To 500 mg. of Co as dry $CoCl_2$ 5 cc. of 27 n. HF and 10 cc. of 6 n. NH_4OH were added: there was a slight turbidity in the pink solution, but this disappeared completely when the solution was heated nearly to boiling.

The experiment was repeated with 500 mg. of Ni as dry $NiCl_2$: there was no precipitate, either in the cold or on heating.

P. 141, N. 2.—Behavior of Indium with Acid Ammonium Fluoride and its Slight Extraction from Cerium Fluoride.—A solution of 100 mg. of In as $InCl_3$ in 0.5 cc. of 27 n. HF and 10 cc. of water was made neutral to litmus with 6 n. NH_4OH: a white curdy precipitate formed. Two drops (0.05 cc.) of 27 n. HF were added: the precipitate dissolved immediately.

To an HF precipitate containing 100 mg. of Ce and 4 mg. of In in a platinum dish 5 cc. of 27 n. HF and 10 cc. of 6 n. NH_4OH were added, and the mixture was heated in the steam-bath for 3 minutes, then cooled and filtered; the filtrate was evaporated with 3 cc. of 95% H_2SO_4 to 0.5 cc., and an excess of 6 n. NH_4OH was added; the resulting precipitate was filtered out, washed, dissolved in 10 cc. of boiling-hot 6 n. $HC_2H_3O_2$, and this solution was saturated with H_2S: a yellow precipitate formed, corresponding to 0.5–1.0 mg. of In.

P. 142, N. 2, 3.—Behavior of Scandium, Titanium, Zirconium, and Rare-Earth Elements towards Concentrated Sulfuric Acid.—0.5 mg. of Sc and 1 mg. of Sc in 5 cc. of 6 n. H_2SO_4 were evaporated till the acid fumed strongly and the volume became about 0.5 cc., and the mixture was allowed to cool: in each case a dense white granular precipitate separated from the hot acid and remained on cooling.

In separate experiments 100 mg. of Ti and 100 mg. of Zr in 5 cc. of 6 n. H_2SO_4 were evaporated till the acid fumed strongly and the volume became 0.5 cc.: no precipitate formed. The solution was cooled: it still remained clear.

Mixtures of 100 mg. of Ti with 1 mg., 1.5 mg., 3 mg., 3.5 mg., and 4 mg. of Sc were treated as in the preceding experiment: no precipitate separated from the mixtures with 1 mg. and 1.5 mg. of Sc; a barely perceptible turbidity appeared in that with 3 mg. of Sc; and precipitates corresponding to about 0.5 mg. and 1.0 mg. of Sc respectively separated from the mixtures with 3.5 and 4 mg. of Sc.

0.5 mg. of Th, 1 mg. of Th, and 0.5 mg. of Fe^{III} were treated separately as in the preceding experiments: a distinct precipitate separated in each case.

0.5 mg. of Ce and 1 mg. of Ce were treated as before: no precipitate separated. 2 mg. of Ce were so treated: a very small crystalline precipitate separated.

3 mg., 4 mg., 5 mg., and 6 mg. of Y were treated as before: there was formed no precipitate in the experiments with 3 and 4 mg., an extremely small one in that with 5 mg., and a much larger one in that with 6 mg.

P. 142, N. 4.—Behavior of Scandium, Zirconium, and Cerium in the Fluoride Confirmatory Test for Scandium.—To 1 mg. of Sc as dry $ScCl_3$ 48% HF solution was added drop by drop, stirring after each addition: with 4 drops a precipitate could be well seen, which was still distinct after 10 drops were added, but there remained only a very slight turbidity after 20 drops had been added.—The last experiment was repeated except that 0.5 cc. of water was added before the HF solution: no precipitate or turbidity appeared either with 4 drops or 20 drops of 48% HF.

To 30 mg. of Sc as dry $ScCl_3$ 15 drops of 48% HF were added: a large gelatinous precipitate formed. 15 drops of 6 n. NH_4OH were then gradually added: the gelatinous precipitate partly dissolved and was partly converted into a finely crystalline one. 2 cc. of water were added: most of the precipitate dissolved. 1 cc. more water was added: a clear solution resulted.

To 5 mg. of Zr as dry $Zr(NO_3)_4$ 4 drops of 48% HF were added: a clear solution resulted.

To 1 mg. of Ce as dry $Ce(NO_3)_3$ 5 drops of water and 10 drops of 48% HF were added: there formed at once a faint turbidity, and upon standing a small coagulated precipitate. 8 drops of 6 n. NH_4OH were added, and the mixture was heated nearly to boiling: the precipitate still remained.

P. 143.—Separation of Thorium from the Rare-Earth Elements by Potassium Iodate.—See R. J. Meyer, *Z. anorg. Chem.*, 71, 65 (1911).

P. 143, N. 1.—Decomposition of Rare-Earth Fluorides by Acids.—To 100 mg. of Th as precipitated ThF_4 2–3 cc. of 95% H_2SO_4 were added, and the mixture was heated till it fumed strongly: there was a white slimy residue. The mixture was cooled, treated with 100 cc. of water, and heated to boiling: all but a slight turbidity dissolved.

In separate experiments 100 mg. of Ce and 100 mg. of Y as precipitated fluorides were heated to fuming with 1 cc. of 95% H_2SO_4: a large white crystalline precipitate separated. The mixture was cooled and diluted with 10 cc. of water: a clear solution resulted.

To 100 mg. of Th as precipitated ThF_4 in a platinum dish 3 cc. of 12 n. HCl were added, and the liquid was evaporated just to dryness, this operation being repeated six times; water was then added, and the mixture was heated to boiling: most of the residue remained.

To 100 mg. of Sc in 35 cc. of 48% HF, 13 cc. of 6 n. NH_4OH, and

35 cc. of water, 7 cc. of 12 n. HCl were added: a large white fine granular precipitate separated. The mixture was evaporated just to dryness; to the residue a little 12 n. HCl was added and this was evaporated off on a steam-bath, these operations being carried out four times in all; the final residue was heated with 50 cc. of cold water on a steam-bath for 15 minutes: a large residue remained.

P. 143, N. 2.—Dissolving of Ytterbium Hydroxide by Acetic Acid.—200 mg. of Yb as precipitated hydroxide were thoroughly washed, and 5 cc. of cold 6 n. $HC_2H_3O_2$ were poured through the filter: the precipitate dissolved readily. H_2S was passed into the solution: no precipitate appeared.

P. 143, N. 5.—Separation of Thorium and Cerium from Other Rare-Earth Elements by Potassium Iodate and Chlorate in Nitric Acid Solution.—Definite quantities of various elements as dry nitrates were separately dissolved in 5 cc. of 16 n. HNO_3, 1 g. of powdered $KClO_3$ was added, the mixture was heated on a steam-bath for 5 minutes, 20 cc. of 0.35 f. KIO_3 solution were then added, and the mixture was cooled with constant agitation, and allowed to stand 10 minutes. The precipitate, if any, was filtered out and washed with 18 cc. of water mixed with 2 cc. of 0.35 f. KIO_3, and the filtrate and washings together were made alkaline with NH_4OH, heated to boiling, and allowed to stand. The KIO_3 precipitate was dissolved in HCl, and the rare earth reprecipitated with NH_4OH. The results are shown in the following table.

Element	Milligrams taken	Milligrams precipitated		Element	Milligrams taken	Milligrams precipitated	
		by KIO_3 and $HClO_3$	*from filtrate by NH_4OH*			*by KIO_3 and $HClO_3$*	*from filtrate by NH_4OH*
Th	½	Ppt.	—	La	100	0	100
	100	100	0		200	80	120[c]
Ce	½	Ppt.	—	Y	100	0	100
	100	100[a]	0		200	10	190
Sc	50	10	40	Yb	100	0	100
					200	0[d]	200
Zr	50	50[b]	0	Ce^{III}	190	0[e]	190

[a] Bright-yellow precipitate.

[b] This precipitate was heated with 35 cc. of 3% H_2O_2 and 10 cc. of 16 n. HNO_3: it dissolved completely. 20 cc. of 0.35 f. KIO_3 were added, and the mixture was let stand 10 minutes: there was a large precipitate. The filtrate was made alkaline with NH_4OH: no precipitate formed.

[c] Determined by igniting and weighing.

[d] Even after 3 hours' standing.

[e] No $KClO_3$ was added, and 20 cc. of 8 n. HNO_3 were used in place of the 5 cc. of 16 n. HNO_3.

To the same treatment were subjected also mixtures of 50 mg. of Th and 50 mg. of Ce with *a*, no other element; *b*, with 1 mg. of La; *c*, with 1 mg. of Pr; and *d*, 1 mg. of Y. In the filtrate from the KIO_3 precipitates NH_4OH produced precipitates corresponding in *a* to less than 0.1 mg. of Ce, and in *b*, *c*, and *d* to about 1 mg. of La, Pr, or Y, respectively. To the last three precipitates suspended in the ammoniacal liquid 3% H_2O_2 was added: they turned only slightly yellow, showing the presence of only very little cerium.

P. 144, N. 1–3.—Separation of Cerium from Thorium as Iodates with the Aid of Hydrogen Peroxide.—100 mg. of Ce as precipitated $Ce(IO_3)_4$ were heated with 35 cc. of 3% H_2O_2, 20 cc. of 0.35 f. KIO_3 solution, and 10 cc. of 16 n. HNO_3 on a steam-bath for 5 minutes: a clear colorless solution resulted. The solution was allowed to stand two hours: a considerable turbidity appeared.

100 mg. of Th as precipitated $Th(IO_3)_4$ were heated with 35 cc. of 3% H_2O_2, 20 cc. of 0.35 f. KIO_3 solution, and 10 cc. of 16 n. HNO_3 for 5 minutes on a steam-bath; the mixture was filtered after standing for 10 minutes, and the filtrate was diluted, made alkaline with NH_4OH and allowed to stand: no precipitate separated.

A mixture of 100 mg. of Th and 1 mg. of Ce as precipitated iodates was treated as in the last experiment: NH_4OH produced a yellow precipitate corresponding to only 0.2 mg. of Ce.

A mixture of 100 mg. of Th and 1 mg. of Ce as precipitated iodates was heated with 35 cc. of 3% H_2O_2 and 10 cc. of 16 n. HNO_3 on a steam-bath for 5 minutes: a considerable part of the precipitate dissolved. Then 20 cc. of 0.35 f. KIO_3 were added; the mixture was cooled, allowed to stand 10 minutes, and filtered; and the filtrate was diluted and made alkaline with NH_4OH: a precipitate corresponding to 0.8 mg. of Ce resulted.

A mixture of 100 mg. of Ce and 1 mg. of Th as precipitated iodates was heated with 35 cc. of 3% H_2O_2 and 10 cc. of 16 n. HNO_3 on a steam-bath for 1 minute: a clear solution resulted. 20 cc. of 0.35 f. KIO_3 were added, the mixture was heated for 4 minutes more, then cooled, and allowed to stand 10 minutes: a small white precipitate corresponding to about 2 mg. separated. It was dissolved in HCl, the solution was evaporated to dryness, and the residue was treated with 2 cc. of water, 2 drops of 6 n. HCl, and 5 cc. of 3% H_2O_2: a white precipitate corresponding to 1 mg. of Th separated. The mixture was filtered, and the filtrate made alkaline with NH_4OH: a yellow precipitate formed corresponding to 1 mg. of Ce.

P. 145.—Test for Thorium with Hydrogen Peroxide.—See Wyrouboff and Verneuil, *Bull. soc. chim.*, (3), 19, 219 (1898).

P. 145, N. 2.—Behavior of Thorium, Cerium, and Zirconium in the Confirmatory Test for Thorium with Hydrogen Peroxide.—To separate solutions of 1 mg. of Th as neutral $ThCl_4$ in 2 cc. of water were added no HCl, 2 drops (0.07 cc.), 4 drops (0.14 cc.), 6 drops (0.20 cc.), and 9 drops (0.30 cc.) of 6 n. HCl; then 5 cc. of 3% H_2O_2 were added to each solution, and it was heated to 60°, and allowed to stand at room temperature: a precipitate separated at once in the cold from the solution containing no HCl, and from that containing 2 drops of HCl; a smaller one separated from that containing 4 drops of HCl, but only after heating to 60° and standing 5–10 minutes, and no precipitate separated from the solutions containing 6 drops and 9 drops of HCl, even on heating and standing 30 minutes.

100 mg. of Ce as neutral $CeCl_3$ were treated with 1 cc. of water and 2½ cc. of 3% H_2O_2, and the mixture was heated at 60° for 10 minutes: a very slight turbidity appeared. One drop of 6 n. HCl was added: the solution became clear. It was allowed to stand two days: no precipitate appeared.

To 50 mg. of Zr as dry chloride 2 cc. of water, 2 drops of 6 n. HCl and 5 cc. of 3% H_2O_2 were added, and the mixture was heated at 60–70° for 5 minutes: no precipitate separated, even on standing 3 hours.

P. 146. N. 1.—Delicacy of the Confirmatory Test for Cerium with Hydrogen Peroxide.—To 0.2 mg. of Ce 60 cc. of water, 2 cc. of 6 n. NH_4OH, and 5 cc. of 3% H_2O_2 were added, and the mixture was gently heated: a distinctly yellow precipitate separated.

P. 147.—Fractionation of Rare Earths by Potassium Carbonate.—See Drossbach, *Ber. d. chem. Ges.*, **33**, 3506 (1900).

P. 147, N. 4.—Action of Potassium Carbonate Solution on a Nickel Crucible.—3 cc. of 50% K_2CO_3 and 20 cc. of water were heated in a covered nickel crucible for two hours on a steam-bath; the solution was then evaporated to dryness with excess of HCl; to the residue were added 10 cc. of water and 3 cc. of 10% $H_2C_4H_4O_6$ solution, and the mixture was made strongly alkaline with NaOH and saturated with H_2S: a brown color corresponding to 0.04 mg. of Ni resulted.

P. 147, N. 5.—Separation of the Lanthanum Subgroup from the Yttrium Subgroup by Potassium Carbonate.—To various quantities of different rare-earth elements as dry chlorides in 3 cc. of 50% K_2CO_3 25 cc. of water were added in one series of experiments, 20 cc. of water in another, and 15 cc. in a third; the mixtures were heated for 2 hours directly in the steam of a steam-bath in 35-cc. nickel crucibles provided with closely fitting covers, and then filtered; the precipitates were dissolved in 6 n. HCl and the solutions made alkaline with 6 n. NH_4OH; the filtrates were acidified with 6 n. HCl, boiled, and made

alkaline with 6 n. NH_4OH; and from the appearance of the precipitates the proportions precipitated and not precipitated by the K_2CO_3 were estimated. The results expressed in milligrams are as follows:

Element	La	La	Pr	Nd	Nd	Nd	Sm	Sm	Gd	Yb	Y
Mg. taken	100	2.0	2.0	2.0	4.0	8.0	8.0	10.0	100	100	100
25 cc. of water added											
Ppted.	99.6	1.9	1.6	0.0	0.0	4.3	0.4	1.5	30	5	7
Not ppted.	0.4	0.1	0.4	2.0	4.0	3.7	7.6	8.5	70	95	93
20 cc. of water added											
Ppted.	—	1.7	1.0	—	0.0	3.6	0.0	0.0	—	1	0
Not ppted.	—	0.3	1.0	—	4.0	4.4	8.0	10.0	—	99	100
15 cc. of water added											
Ppted.	—	0.0	0.0	—	—	—	—	—	—	—	—
Not ppted.	—	2.0	2.0	—	—	—	—	—	—	—	—

The experiments were repeated with mixtures of 100 mg. of La with certain quantities of erbium and yttrium, using 25 cc. of water: the results were as follows (that with the 100 mg. of La and 50 mg. of Y being obtained by precipitating, igniting, and weighing the yttrium present in the filtrate from the K_2CO_3 precipitate):

Element	Er	Y	Y
Mg. taken	8	8	50
Mg. in filtrate	$2\frac{1}{2}$	$1\frac{1}{2}$	35

P. 148.—Fractionation of Rare Earths by Formate.—See Meyer and Müller, *Z. anorg. Chem.*, 109, 17 (1919).

P. 148, N. 3.—Separation of the Lanthanum Subgroup from the Yttrium Subgroup by Ammonium Formate.—To various quantities of the different rare-earth elements, each taken separately in the form of dry acid-free chloride or nitrate, in a test-tube 1.5 cc. of 95% $HCHO_2$ (s. g., 1.22) were added, the mixture was agitated or warmed slightly till complete solution took place, then 5 cc. of 6 n. NH_4OH were added, the mixture was heated nearly to boiling, then cooled and allowed to stand for 10 minutes. The results are as follows:

Element	La	La	Pr	Pr	Nd	Nd
Mg. taken	0.5	1.0	0.5	1.0	1.0	1.5
Precipitate	yes	yes	slight	yes	none	slight
Element	Nd	Sm	Sm	Sm	Gd	Gd
Mg. taken	2.0	3.0	5.0	8	6	50
Mg. in precipitate	yes	0.0	0.3	5	0	0

In the four cases where no precipitate separated in 10 minutes, this was still true also after standing for 12 hours. The division of the samarium between precipitate and solution was estimated in the way described in the next experiment.

100 mg. of various rare-earth elements were treated by the process just described; then, after the 10 minutes' standing, the mixtures, when any precipitate had separated, were filtered; and the quantities of the element present in the precipitate and filtrate were estimated from the appearance of the precipitates obtained by dissolving the precipitate in 6 n. HCl and adding 6 n. NH_4OH to the solution, and by evaporating the filtrate to dryness with 6 n. HNO_3 and adding water and NH_4OH to the residue. The numbers of milligrams found in the precipitate and filtrate are shown in the following table. The erbium, ytterbium, and yttrium solutions gave no precipitate even after three days.

Element	La	Pr	Nd	Sm	Gd	Er	Yb	Y
Mg. in precipitate	99.7	99.0	98.5	97.5	35	0	0	0
Mg. in filtrate	0.3	1.0	1.5	2.5	65	100	100	100

100 mg. of Er, 100 mg. of Yb, and 100 mg. of Y were separately treated as in the first experiment, except that only 0.5 cc. of 95% $HCHO_2$ and 1.0 cc. of 6 n. NH_4OH were added (making the total volume 23% and the NH_4CHO_2 concentration 87% of that in the previous experiments): even under these conditions no precipitate separated in the ytterbium or yttrium solutions in three days, nor in the erbium solution in half an hour; but in the last solution a considerable pinkish precipitate had separated after 12 hours.

Mixtures of 100 mg. of La with various quantities of different elements of the yttrium subgroup were treated as in the first experiment, the precipitates being filtered out after 10 minutes' standing, and the filtrates being evaporated with HNO_3 and the residues treated with water and NH_4OH; the quantities of the yttrium subgroup element passing into the filtrate were estimated from the size of the precipitate (in the case of the experiment with 50 mg. of La and 100 mg. of Y more exactly by igniting it and weighing the residue), subtracting from the total quantity 0.3–0.5 mg. representing the quantity of lanthanum which passes into the filtrate. The results are as follows:

Element	Gd	Gd	Er	Er	Yb	Y	Y	Y	Y
Mg. taken	4	8	4	8	4	2	4	8	50
Mg. in filtrate	0	0	0	0.5	0.5	0	0.5	1.5	20

A mixture of 100 mg. of Y and 1 mg. of La as dry chlorides was treated as in the first experiment: a small crystalline precipitate appeared after 10 minutes' standing, and this became larger after 30 minutes, then appearing to be only a little smaller than that produced by 1 mg. of La alone.

P. 149.—Separation of Prascodymium from Other Rare-Earth Elements by Fusion with Sodium Nitrate.—See Brauner, *Proc. Chem. Soc. London*, 17, 66 (1901); Meyer, *Z. anorg. Chem.*, 41, 97 (1904).

P. 149, N. 6.—Behavior of Praseodymium, Lanthanum, Neodymium, and Samarium on Fusion with Sodium Nitrate.—Various quantities of the nitrates of these elements, taken separately, were intimately mixed with 7 g. of $NaNO_3$ in a 30-cc. porcelain crucible, the crucible was covered, and the mixtures were fused for definite lengths of time, at various definite temperatures. Constant temperature was attained either by placing the crucible in the vertical chamber of a well-insulated electric furnace provided with a copper-constantan junction, or by heating it (at 445°) in a vertical tube within a jacket filled with the vapors of boiling sulfur. After the melt had cooled it was extracted with about 20 cc. of cold water; and any residue was then agitated for 15–30 minutes with a mixture of 8 cc. of 1 n. $HC_2H_3O_2$ and 40 cc. of 1 n. $NaC_2H_3O_2$ solution. The proportions of the element in the aqueous extract, in the acetate solution, and in the residue (after dissolving it in hydrochloric acid) were estimated by precipitating the hydroxide with ammonium or sodium hydroxide, and estimating the amount of the precipitates from their appearance, or in a few cases against which a Q is placed by igniting them and weighing the resulting oxide. The data are given in the following tables.

Experiments with 100 mg. of praseodymium

Expt. No.	1	2	3	4	5	6	7	8	9	10	11
Temperature	570	510	460	460	460	445	445	445	445	445	445
Hours heated	1	1½	1	1½	2	1½	2½	3	3	4	5
Mg. in water extract	0	0	15	0	0	45	8	4	5	5	0
Mg. in acetate solution	1	2[a]	{ 85 }	1½	1½	{ 55 }	{ 92 }	4	{ 95 }	{ 95 }	1
Mg. in residue	99	98		98½	98½			92			99

Experiments with 100 mg. of lanthanum

Expt. No.	12	13	14	15	16	17	18	19	20	21
Temperature	570	510	460	460	460	465	445	445	445	445
Hours heated	1	1½	1	1½	2	1½	3	3	3	3
Mg. in water extract	7	0	95	87	70	70	64.1	91	82	88.0
Mg. in acetate solution	90	98[a]	{ 5 }	12	28	9	6.5Q	5	10	9.0Q
Mg. in residue	3	2		1	2	21	29.4Q	4	8	3.0Q

Experiments with 100 mg. of other rare-earth elements

Expt. No.	22	23	24	25	26	27	28	29	30	31
Element	Nd	Nd	Nd	Nd	Sm	Sm	Sm	Gd[b]	Yb	Y
Temperature	515	460	445	445	460	463	510	510	510	510
Hours heated	1½	1½	5	5	1½	1½	1½	1½	1½	1½
Mg. in water extract	0	20	38	54	59	12	0	0	0	0
Mg. in acetate solution	94[a]	79½	60	44	40	88	94[a]	49½	30[c]	30[c]
Mg. in residue	6	½	2	2	1	0	6	½	70	70

[a] After 5 hours' rotation with acetate mixture. [b] 50 mg. of Gd and 3½ g. of $NaNO_3$ were used.
[c] After 5 hours' rotation with acetate mixture. After rotating 16 hours longer 30 mg. more were dissolved.

Experiments with Mixtures of Lanthanum, Praseodymium, and Neodymium

Expt. No.	32		33		34		35	
Temperature	460		460		460		460	
Hours heated	1½		1½		1¾		1½	
Element	Pr	La	Pr	La	Pr	La	Pr	La
Mg. taken	100.0	3.0	3.0	100.0	3.0	100	10.0	100
Mg. in water extract	0.02	0.3	0.1	86.3	0.3	69	0.5	90
Mg. in acetate solution	1.7	0.8	2.8	12.2	2.5	27	9.0	3
Mg. in residue	98.3	1.9	0.1	1.5	0.2	4	0.5	7

Expt. No.	36		37		38		39	
Temperature	445		445		460		500	
Hours heated	5		5		1½		1	
Element	Pr	La	Pr	La	Pr	La	Pr	La
Mg. taken	100.0	3.0	3.0	100	10.0	10.0	10.0	100
Mg. in water extract	0.5	0.5	1.8	89	0.1	5.9	0.5	30
Mg. in acetate solution	1.5	1.5	1.0	9	4.2	1.8	9.3	65
Mg. in residue	98.0	1.0	0.2	2	5.7	2.3	0.2	5

Expt. No.	40		41		42	
Temperature	463		460		460	
Hours heated	1½		1½		1½	
Element	Pr	La	Pr	La	Pr	La
Mg. taken	100.0	3.0	100.0	6.0	100.0	10.0
Mg. in water extract	0.3	0.9	0.6	2.4	2.0	8.0
Mg. in acetate solution	2.7	0.3	4.5	0.5	4.5	0.5
Mg. in residue	97.0	1.8	95.0	3.1	93.5	1.5

Expt. No.	43		44		45		46	
Temperature	463		463		463		445	
Hours heated	1½		1½		1½		5	
Element	Pr	Nd	Pr	Nd	Pr	Nd	La	Nd
Mg. taken	3	100	100	3.0	100	6.0	50	50
Mg. in water extract	3[a]	17	0	0.0	0	0.0	47	28
Mg. in acetate solution	3[a]	81	2[c]	0.8[c]	2[c]	0.8[c]	1[b]	21[b]
Mg. in residue	0	2[d]	98	2.2	98	5.2	3	

[a] This was the quantity in the water extract and acetate solution combined.

[b] The proportions of lanthanum and neodymium in the acetate solution were determined by heating the hydroxides with 20 cc. of 50% K_2CO_3 diluted with 160 cc. of water.

[c] On adding NH_4OH a yellowish-white precipitate resulted.

[d] This residue was almost white.

P. 149, N. 8.—Modifications of the Sodium Nitrate Fusion for Separating Praseodymium, Lanthanum and Neodymium.—a. Effect of Passing Oxidizing Gases through the Melt.—The experiments whose results are presented in the following tables were made by passing the gas indicated in the heading at a rate of about one bubble per second for three hours (unless otherwise stated) through a perforated crucible-cover into the fused mass heated in a porcelain crucible to 445°. The mass consisted of 7 g. of $NaNO_3$ and 100 mg. of the stated element in the form of nitrate. The determinations against which a Q is placed were made quantitatively by igniting and weighing the oxide. The oxygen or nitrous oxide was first dried with 95% H_2SO_4.

Oxygen-gas experiments with 100 mg. of lanthanum

Expt. No.	19–21[a]	47	48[b]	49[b]	50
Mg. in water extract	87	80.6	79.3	77.8	80½
Mg. in acetate solution	8	17.0Q	17.0Q	19.0Q	1½
Mg. in residue	5	2.4Q	3.7Q	3.2Q	18Q

Oxygen-gas experiments with 100 mg. of praseodymium

Expt. No.	8–9[c]	51	52	53	54	55	56
Hours heated	3	3	3	3	3	2	1½
Mg. in water extract	4½	0	0	0	1½	4	18

[a] Mean results of expts. no. 19, 20, 21 in which *no gas* was passed.
[b] In these cases the fused mass was heated in a nickel crucible.
[c] Mean results of expts. no. 8 and 9 in which *no gas* was passed.

Oxygen-gas experiments with mixtures of lanthanum and praseodymium and with neodymium and samarium alone

Expt. No.	57		58		59	60
Element	Pr	La	La	Pr	Nd	Sm
Mg. taken	100	3	100	3	100	100
Mg. in water extract	0	3	60		43½	40
Mg. in acetate solution	5	0	3		55	58½
Mg. in residue	95	0	40		1½	1½

In other experiments air was first passed through 16 n. HNO_3 at 0° or at 22° or through fuming HNO_3 at 22° of sp. gr. 1.60, and it was then conducted into the fused mass kept at 445° in a sulfur bath for three hours. 100 mg. of lanthanum or of praseodymium were used in each case.

Experiments with Air Charged with Nitric-Acid Vapors

Expt. No.	18	61	62	63	64	65
Nitric acid used	None	16 n.	16 n.	16 n.	16 n.	Fum.
Temperature of acid	—	0°	0°	22°	22°	22°
Element	La	La	La	La	Pr	La
Mg. in water extract	64	70	71	61	1	65
Mg. in acetate solution	6.5Q	27	2	2	3	7
Mg. in residue	29.4Q	3	27Q	37	96	28Q

Nitrous Oxide Experiments with 100 mg. of Praseodymium

Expt. No.	66	67	68	69	70	71	72	54
Hours heated	1½	2	2½	2½	2½[a]	3	3	3[b]
Mg. in water extract	18	10	1½	1½	10	1½	1½	1½

[a] In this experiment the N_2O was passed at the rate of 150 bubbles instead of 60 bubbles per minute. The more rapid current probably lowered the temperature of the fusion.

[b] This experiment was made with oxygen, in place of nitrous oxide, so as to furnish a direct comparison.

Nitrous Oxide Experiment with a Mixture of Lanthanum and Praseodymium

Expt. No.	73	
Element	La	Pr
Mg. taken	100	3
Mg. in water extract	67Q	1
Mg. not dissolved by water	33Q	2

Into a fused mixture of 3.5 g. of $NaNO_3$ and 4.0 g. of KNO_3 with 100 mg. of Pr as nitrate kept at 235–239° in an electric oven was passed for three hours at the rate of 20 bubbles per second oxygen gas containing ozone, prepared by the electrolysis of ice-cold 3 n. H_2SO_4 using a rapidly rotated short thin platinum wire as an anode and a current of 3.5 amperes, somewhat as described by Fischer and Massenez, *Z. anorg. Chem.*, **52**, 202 (1907), the ozone content of the gas being such that the quantity passed in 3 hours was about 0.04 mol of O_3: the melt showed no trace of brown color or brown precipitate.

The same ozonized oxygen was passed at 22° into 15 cc. of a neutral aqueous solution containing 50 mg. Pr as $Pr(NO_3)_3$: no brown precipitate resulted. The solution was then made slightly acid and afterwards slightly alkaline, and the ozonized oxygen was again passed into it: in each case no precipitate formed. It was heated to 100° and the gas again passed into it: still no precipitate formed.

b. Effect of Adding Solid Oxidizing Agents to the Melt.—A mixture of 7 g. of $NaNO_3$ and 0.5 g. of $AgNO_3$ with 100 mg. of La as

nitrate was heated for 3 hours at 445°; the aqueous extract and the residue from it were treated with HNO_3, and the solutions were made alkaline with NH_4OH: the extract was thus shown to contain 75 mg. and the residue 25 mg. of La.

A mixture of 7 g. of $NaNO_3$ and 0.25 g. of Na_2O_2 with 100 mg. of La was heated at 430–450° for one hour; and the melt was then treated as usual: the aqueous extract, which was strongly alkaline, contained no lanthanum; the acetate solution, which was rotated with the residue for 12 hours, contained 85 mg., and the residue from it contained 15 mg., of lanthanum.—The last experiment was repeated, replacing the 100 mg. of La by 100 mg. of Pr: the quantity of praseodymium in the aqueous extract was 0 mg.; that in the acetate solution, 20 mg.; and that in the residue from it, 80 mg.

With an intimate mixture of 7 g. of $NaNO_3$ and 0.5 g. of bismuth dioxide ("sodium bismuthate"), previously washed with HNO_3, were mixed 100 mg. of Pr in one experiment, and 100 mg. of La in another experiment, this being dissolved in 2 drops of HNO_3, in a porcelain crucible. This mixture was heated for one hour at 445°. The melt was extracted with water, the solution acidified, H_2S passed in, the liquid filtered and boiled, and NH_4OH added. The residue from the aqueous extract was treated with the acetate mixture in the usual way; the precipitate obtained from it by adding NH_4OH was dissolved in dilute HCl, and the solution was treated with H_2S, filtered, boiled to expel H_2S, and made alkaline with NH_4OH. The residue from the acetate treatment was treated in the same way. The rare-earth element was estimated to have divided itself in the following way:

Element	Pr	La
Mg. taken	100	100
Mg. in water extract	18	25
Mg. in acetate solution	57	65
Mg. in residue	25	10

c. Incidental Effects Attending the Sodium-Nitrate Fusion.—Reaction of the Aqueous Extract towards Litmus.—The aqueous extract of the $NaNO_3$ fusion was in many experiments tested with litmus paper: it was always perfectly neutral, except in the cases where HNO_3 vapor had been passed through the melt, when it was very faintly acid.

Production of Nitrite.—The nitrite present in the aqueous extract was determined in several experiments where the melt had been heated at 445° while passing oxygen for three hours, by acidifying with H_2SO_4, and titrating with 0.05 n. $KMnO_4$: the number of milligrams of $NaNO_2$ formed were as follows:

9 mg. with 7 g. of $NaNO_3$ + 100 mg. of Pr
9 mg. with 7 g. of $NaNO_3$ + 100 mg. of Pr + 3 mg. of La
0.8 mg. with 7 g. of $NaNO_3$ + 100 mg. of La
1.6 mg. with 7 g. of $NaNO_3$ + 100 mg. of La + 3 mg. of Pr

In the experiments (nos. 44 and 45) with 100 mg. of Pr + 3 mg. of Nd and with 100 mg. of Pr + 6 mg. of Nd where no gas was passed, 18 mg. of $NaNO_2$ were produced in each experiment.

Action on the Crucible.—7 g. of $NaNO_3$ were heated in a porcelain crucible at 460° for 1½ hours; the melt was then dissolved in water, and the solution made alkaline with NH_4OH: the aqueous solution was perfectly clear and neutral, and gave no precipitate with NH_4OH.

Composition of the Crystalline Lanthanum Compound Produced in the Nitrate Fusion.—The residue obtained by a fusion of 100 mg. of La at 445° for 3 hours with oxygen bubbling (Expt. 50), after extracting with water and with acetate solution was washed thoroughly, rinsed into a porcelain crucible, dried for 15 hours at 110°, weighed, ignited, and weighed again: the dried residue weighed 26.3 mg. and the ignited residue 25.2 mg., showing that the dried residue was La_2O_3, containing only a very small quantity of H_2O or N_2O_5.

Indications of the Presence of Praseodymium Afforded by the Color of the Fusion.—3 mg. of Pr were heated with 7 g. of $NaNO_3$ at 460–465° for 1½ hours: while the melt was liquid a fine brownish-black powder was seen in the bottom of the crucible.—A mixture of 3 mg. of Pr and 100 mg. of La were heated with $NaNO_3$ in the same way: no dark particles separated, but the melt became slightly reddish.

d. Behavior of Praseodymium and Lanthanum on Fusion with Sodium Nitrite.—With 7 g. of powdered $NaNO_2$ 100 mg. of Pr as dry $Pr(NO_3)_3$ were intimately mixed, and the mixture was heated at 445° in a sulfur-bath in a porcelain crucible for three hours; the melt was then treated with 100 cc. of cold water, and the undissolved part was shaken with the usual acetate mixture for 15 minutes: the aqueous extract was alkaline and contained no praseodymium; the acetate solution contained 15 mg. of Pr; and the light-brown residue insoluble in it contained 85 mg. of Pr.

The experiment was repeated, using 100 mg. of La in place of the 100 mg. of Pr: the acetate solution contained 17 mg. of La and the residue 83 mg. of La.

e. Behavior of Praseodymium on Fusion with Sodium Perchlorate and Sodium Chloride.—An intimate mixture of 2.5 g. of $NaClO_4$, 0.5 g. of NaCl, and 10 mg. of Pr as $PrCl_3$ was heated in a hard-glass tube (provided with a gas delivery tube) at 445° in a sulfur-bath for 1½ hours: 212 cc. of oxygen gas had then been given off, and the melt consisted of a considerable quantity of reddish-white solid and of a small quantity of liquid. The melt was then heated for 1½ hours more: 171 cc. more oxygen were given off, and the appearance of the melt was about the same as before. It was treated with cold water,

the mixture was filtered, and the (slightly acid) filtrate was made alkaline with NH_4OH: a precipitate corresponding to 4 mg. of Pr resulted, 6 mg. of Pr being therefore left in the undissolved residue.

P. 149, N. 9.—Separation of Lanthanum and Neodymium by Potassium Carbonate Solution.—To 20 cc. of 50% K_2CO_3 solution were added in separate experiments the quantities of lanthanum or neodymium shown below; then 160 cc. of water were added; and the mixture was heated for two hours on a steam-bath in a large platinum dish covered with a watch-glass, the water that evaporated being replaced from time to time; the solution was then filtered, the precipitate (which in the lanthanum experiments consisted of fine compact particles adhering to the sides of the dish) was dissolved in HCl, the solution was made alkaline with NH_4OH, and from the size of the precipit te (compared with that obtained from the K_2CO_3 solution by acidifying, boiling, and adding NH_4OH) the quantity of the rare-earth element precipitated by the K_2CO_3 treatment was estimated to be that shown in the following table:

Expt. No.	1	2	3	4	5	6	7		8	
Element	La	La	La	La	Nd	Nd	La	Nd	La	Nd
Mg. taken	4.0	3.0	2.0	2.0	20	25.0	2.0	20.0	20	20
Mg. ppted.	2.8	2.3	0.3	0.1	0	0.5	1.1[a]	0.4[a]	19	14
Mg. not ppted.	1.2	0.7	1.7	1.9	20	24.5	0.9	19.6	1[b]	6[b]

[a] The proportions of lanthanum and neodymium in the precipitate were determined by heating it with 3 cc. of 50% K_2CO_3 solution and 24 cc. of water on a steam-bath for two hours in a nickel crucible, the precipitate thus formed being considered to be lanthanum.

[b] The proportions of lanthanum and neodymium in the filtrate from the K_2CO_3 precipitate were determined by separating the rare earth from it as hydroxide and heating this with 6 cc. of 50% K_2CO_3 solution and 50 cc. of water on a steam-bath for two hours in two nickel crucibles, the precipitate thus formed being considered to be lanthanum.

P. 149, N. 13.—Colors of Ignited Mixtures of the Oxides of Praseodymium and Lanthanum and of Praseodymium and Neodymium.—Solutions containing various known quantities of praseodymium and lanthanum were precipitated with NH_4OH, the precipitates were filtered out on washed filters, washed thoroughly with water, and ignited in open porcelain crucibles in an inclined position to a low-red heat over a gas flame; the colors were compared with that of mixtures made by grinding intimately together (Baker's) powdered cocoa and powdered sodium chloride in various proportions by volume. These experiments led to the results given in the following table, in which the values in the last row show the volume-percent of cocoa which

imparted about the same color to the mixture of it with the salt as the praseodymium imparted to the mixed oxide when the weight-percent of it (referred to the sum of the rare-earth elements present as 100) had the value given in the first row.

Percent of Pr	2	5	10	15	25
Percent of Cocoa	3	10	18	50	100

The mixtures with 50% and 75% of Pr were proportionally intermediate in shade between the greyish-black of pure PrO_2 and the cocoa-brown color of the mixture with 25% of Pr.

Similar oxide mixtures were made with praseodymium and neodymium; the 50% mixture had nearly the same color as the 50% mixture with lanthanum; but owing to the blue color of Nd_2O_3 the shade of the neodymium mixtures with less than 50% of Pr was much less reddish than that of the lanthanum mixtures, the former being a greyish-brown, instead of a reddish-brown shade.

ANALYSIS OF THE ALKALINE-EARTH GROUP

P. 151, N. 1.—Precipitation of Potassium in Presence of Perchlorate by Ammonium Carbonate and Alcohol.—To 100 mg. of K as KNO_3 and 1 cc. of 9 n. $HClO_4$ in 10 cc. of solution were added 15 cc. of 6 n. $(NH_4)_2CO_3$ and 15 cc. of 95% C_2H_5OH: a crystalline precipitate of $KClO_4$ separated at once.

P. 151, N. 2.—Decomposition of Perchlorate by Ignition with Ammonium Salts.—4 cc. of 3 n. NH_4Cl and 12 n. NH_4OH in excess were added to 3 cc. of 9 n. $HClO_4$ containing 100 mg. of potassium as KNO_3, and the mixture was evaporated until it bumped badly; the flame was then caused to play on the residue in the casserole till it was decomposed: scarcely any fumes of ammonium salt came off; the reaction started at isolated points, and spread through the residue, raising the adjacent material to incandescence. After cooling, the residue was dissolved in 10 cc. of water, and treated with 15 cc. of 6 n. $(NH_4)_2CO_3$ reagent and 15 cc. of C_2H_5OH; on standing a slight precipitate separated, but this was proved to be only silica; showing that perchlorate, even in presence of potassium, is mostly destroyed by the ignition with ammonium salts.

A mixture of 1 g. of KCl, 5 g. of NH_4Cl, 2 cc. of 9 n. $HClO_4$, and 10 cc. of water was evaporated to dryness and heated as in the preceding experiment; 3 g. of NH_4Cl and a little water were added, and the process was repeated; the residue was then treated with 15 cc. of 6 n. $(NH_4)_2CO_3$ and 15 cc. of C_2H_5OH: no precipitate formed in 30 minutes, showing that most of the perchlorate had been destroyed.

In five experiments, to a mixture of 3 cc. of 9 n. $HClO_4$, 10 cc. of 95% C_2H_5OH, and 10 cc. of 12 n. HCl in a casserole was added 15 n. NH_4OH in small excess, and the mixture was evaporated to dryness (in some experiments on a steam-bath and in others over a free flame); the casserole was now heated over a free flame, gently at first and then at a higher temperature, till no residue remained in the casserole: in no case was there any explosive action, though occasionally a portion of the solid glowed.

P. 151, N. 3.—Non-Volatilization of Cesium.—To 1 mg. of Cs as $CsNO_3$ in 3 cc. of 9 n. $HClO_4$ and 4 cc. of 3 n. NH_4Cl, an excess of 6 n. NH_4OH was added, and the solution was saturated with H_2S and evaporated to dryness. The heating was continued by allowing a flame to play into the dish till all the perchlorate was decomposed and till fumes of ammonium salts were no longer given off. 2 cc. of 3 n. NH_4Cl were then added, and the solution again evaporated and ignited. The residue was dissolved in a little water and 1–2 cc. of silico-

tungstic acid were added: there was an immediate white precipitate, showing that the cesium had not been volatilized.

P. 151, N. 4.—Precipitation of Barium, Strontium, Calcium, and Magnesium by Ammonium Carbonate and Ethyl Alcohol.—As to magnesium see Gooch and Eddy, *Am. J. Sci.*, (4), **25**, 444 (1908); *Z. anorg. Chem.*, **58**, 427 (1908); also Gooch's *Methods in Chemical Analysis*, 155 (1912).

In the following paragraphs are briefly presented most of the experiments made by Bray, *J. Am. Chem. Soc.*, **31**, 625 (1909).

In a series of experiments, to various elements as nitrates 5 cc. of 6 n. HCl were added, this was neutralized with NH_4OH, the solution was brought to a volume of 10 cc., 30 cc. of 6 n. $(NH_4)_2CO_3$ reagent and 30 cc. of 95% C_2H_5OH were added, and the mixtures were frequently shaken: a pronounced turbidity resulted after 5 minutes with 2 mg. of Ba, Sr, Ca, or Mg; after 20 minutes with 0.5 mg. of Ba, 15 minutes with 0.5 mg. of Sr, 10 minutes with 0.5 mg. of Ca, 20–30 minutes with 0.5 mg. of Mg; and after 30 minutes with 0.3 mg. of Mg.

Similar experiments were made with 500 mg.; the mixtures were filtered after 30 minutes, and the quantities still unprecipitated were estimated by evaporating the filtrates and testing the residue for barium and strontium with H_2SO_4, for calcium with NH_4OH and $(NH_4)_2C_2O_4$, and for magnesium with NH_4OH, Na_2HPO_4, and C_2H_5OH: the quantities found were 0.0 mg. of Ca, less than 0.1 mg. of Ba and Mg, and 0.2 mg. of Sr.

To determine the effect of shaking, two other experiments were made with 500 mg. of Mg, but in one case the mixture was filtered after 15 minutes (instead of 30 minutes), and in the other case it was allowed to stand 30 minutes without being shaken (except at the beginning): on letting the filtrates stand 24 hours, 1–2 mg. of Mg separated in the first case, and 2–3 mg. in the second.

To determine the effect of the addition of C_2H_5OH, the experiment with 500 mg. of Mg was repeated several times, except that 10–20 cc. of C_2H_5OH were added, instead of 30 cc.; the mixtures were filtered after half an hour and allowed to stand over night: precipitates formed corresponding to several milligrams of magnesium, the amounts increasing rapidly as the amount of alcohol decreased. The experiments with 0.5–2.0 mg. of each element were repeated, except that no alcohol was added: with barium the precipitates formed as quickly as in the presence of alcohol, and with strontium almost as quickly; but in the experiments with 0.5 and 1.0 mg. of Ca or Mg no precipitates resulted.

To determine the effect of dilution, experiments were made with 0.5 and 1.0 mg. of each element, but making the volume of the solution to which the $(NH_4)_2CO_3$ reagent was added 20 cc., instead of 10 cc.: the solutions became turbid somewhat less quickly, the difference being most marked in the case of magnesium, indicating that 0.5 mg. might escape detection if the volume were still greater.

For the results of experiments under other experimental conditions see Bray, *J. Am. Chem. Soc.*, **31**, 626–627 (1909).

P. 151, N. 5.—Precipitation of Lithium and Potassium by Ammonium Carbonate and Ethyl Alcohol.—150 mg. of Li as LiCl were treated exactly as described in the first experiments under Note 4 above: after half an hour the solution was perfectly clear and there was no precipitate; after 5 hours there was a precipitate, which was smaller than that obtained with 0.5 mg. of Mg. The experiment was repeated with 200 mg. of Li: a granular precipitate separated very slowly which was very small in 30 minutes, but after 24 hours was estimated to contain 20–40 mg. of Li.

As to the precipitation of potassium with magnesium see Gooch and Eddy, *Am. J. Sci.*, (4) **25**, 444 (1908).

P. 151, N. 6.—Behavior of Lithium in the Analysis of the Alkaline-Earth Group.—100 mg. of Li as LiCl were dissolved in $HC_2H_3O_2$ and treated by P. 152–158: no precipitate whatever was obtained in the tests for barium, strontium, and magnesium, and only a very small one corresponding to 0.2–0.4 mg. in that for calcium, which was doubtless due to the presence of calcium as an impurity.

P. 152–158.—Analysis of the Alkaline-Earth Group.—For many confirmatory experiments see Bray, *J. Am. Chem. Soc.*, **31**, 627–632 (1909).

ANALYSIS OF THE ALKALI GROUP

GENERAL DISCUSSION

D. 163.—Perchlorate Separation of the Alkali Elements in Presence of Ethyl Acetate.—500 mg. of Na as $NaNO_3$ and 1 mg. of K as KNO_3 were heated with 3 cc. of 9 n. $HClO_4$: the mixture did not fume, but became practically solid. 3 cc. more of 9 n. $HClO_4$ were added, and the mixture was heated to fuming: on cooling it solidified. 20 cc. of ethyl acetate were added: considerable salt remained undissolved. 5 cc. more ethyl acetate were added, and the mixture was shaken for a few minutes: there was only a small residue. This was filtered off and tested for potassium with $Na_3Co(NO_2)_6$: a yellow precipitate resulted.

100 mg. of Li as LiCl were heated with 3 cc. of 9 n. $HClO_4$ to fuming; 25 cc. of ethyl acetate were added: there was no precipitate. The solution was saturated with dry HCl gas, and let stand several hours: there was no precipitate.

1 mg. of Cs as $CsNO_3$ was heated to fuming with 3 cc. of 9 n. $HClO_4$. After cooling, 25 cc. of ethyl acetate were added: even after standing 1 hour there was no precipitate.

The experiment was repeated using 1 mg. of Rb: a small precipitate separated in a few minutes.

D. 165.—Conversion of Potassium Perchlorate into Chloride by Ignition.—500 mg. of K as $KClO_4$ were heated in a 20-cm. long, 2.5-cm. wide, thick-walled pyrex test-tube till gas ceased to be given off and the mass solidified; the residue was then brought to and kept in a state of fusion for 3 minutes by heating it to the maximum temperature of a Bunsen burner, the whole lower third of the tube being finally strongly heated. After cooling the mass was extracted with 6 cc. of ice water: there was a residue of $KClO_4$ estimated to contain 25 mg. of K.

The experiment was repeated using 100 mg. of K instead of 500 mg.: there was a residue of $KClO_4$ corresponding to 10 mg. of K.

Volatilization of Potassium and Cesium in the Ignition of their Perchlorates.—The experiment just described was repeated with a mixture of 500 mg. of K as $KClO_4$ and 1 mg. of Cs as $CsNO_3$; to the 6 cc. of aqueous extract of the melt was added silicotungstic acid reagent: a large precipitate resulted, showing that little, if any, of the cesium had been volatilized.

The experiment was repeated with a mixture of 100 mg. of K as $KClO_4$ and 0.4 mg. of Cs as $CsNO_3$: after standing in ice water for some minutes a precipitate separated half as large as that obtained

directly with 0.4 mg. of Cs, showing that there had been partial, but not complete, volatilization of the cesium.

A mixture of 1 mg. of K and 1 mg. of Cs as perchlorates was heated in a pyrex tube to the highest temperature of a Bunsen burner for 3 minutes: fumes steadily escaped from the mouth of the tube. The residue was evaporated with a few drops of 6 n. HNO_3, then dissolved in 2 cc. of 10 n. $NaNO_2$, 0.5 cc. of $Bi(NO_3)_3$ reagent was added, and the mixture let stand in ice water: a precipitate corresponding to 0.5 mg. of Cs separated. To the filtrate were added 2 cc. of 1 n. $HC_2H_3O_2$ and 1 cc. of 4 n. $Co(NO_3)_2$: a precipitate resulted five times as large as that given in a control with 2 cc. of the $NaNO_2$ reagent and nearly as large as that given directly by 1 mg. of K.

D. 169.—Non-Extraction of Rubidium from a Large Quantity of Potassium Chloride by Hydrochloric Acid.—500 mg. of K as $KClO_4$ and 1 mg. of Rb as RbCl were fused till the perchlorate was completely changed to chloride; the melt was broken up as fine as possible with a glass rod, and then extracted with 4 cc. of 12 n. HCl; the extract was evaporated to dryness, and the residue so obtained converted to nitrite and treated with $Na_3Bi(NO_2)_6$: no precipitate resulted.

A solution containing 500 mg. of K as KCl and 2 mg. of Rb as RbCl was evaporated to dryness; the residue was extracted with 4 cc. of 12 n. HCl, and the resulting solution evaporated to dryness; the chlorides in this residue were transformed into nitrites by treatment with $AgNO_2$; the nitrite residue was dissolved in 1 cc. of 10 n. $NaNO_2$, treated with 4 drops of $Bi(NO_3)_3$ reagent, and allowed to stand 1 hour in ice water: there was a turbidity but not distinct precipitate. The mixture stood over night at room temperature: a precipitate corresponding to less than 0.2 mg. of Rb settled out.

D. 169.—Behavior of Potassium with Chloroplumbic Acid.—5 cc. of 12 n. HCl were completely saturated with KCl, then with Cl_2 gas, 3 cc. of H_2PbCl_6 reagent (consisting of 12 n. HCl saturated simultaneously with $PbCl_2$ and Cl_2) were added, and the mixture was let stand over night: only a small *white* precipitate separated.

Precipitation of Rubidium and Cesium by Chloroplumbic Acid.—As to the solubility of the chloroplumbates, see Wells, *Am. J. Sci.*, (3), **46**, 184–187 (1893).

Rubidium or cesium in 1% solution as chloride was added, 1 mg. at a time, till precipitation occurred, to mixtures which then had the composition shown below. The number of milligrams required to produce precipitation are shown in the last two columns:

½ cc. of H_2PbCl_6 reagent, 12 cc. of water	100 Rb	—
½ cc. of H_2PbCl_6 reagent, 5½ cc. of water	—	6 Cs
½ cc. of H_2PbCl_6 reagent and 5 cc. of 12 n. HCl saturated with Cl_2	5 Rb	1 Cs
5½ cc. of H_2PbCl_6 reagent	1 Rb	1 Cs

To 4-cc. portions of 12 n. HCl containing 0.5, 1.0, and 2.0 mg. of Rb as RbCl, 2 cc. of H_2PbCl_6 reagent were added, the mixture was saturated with Cl_2 gas, corked, and allowed to stand: with 0.5 mg. and 1.0 mg. of Rb there was no precipitate even after 60 minutes; with 2 mg. of Rb there was a precipitate after 5 minutes, which had become larger after 15 minutes.

PROCEDURES AND NOTES

P. 161, N. 2, 3.—Impurities Introduced from Reagents and by Action on the Vessels in the Course of the Analysis.—10 cc. of 9 n. HBr and 3 drops of liquid Br_2 were evaporated to 0.5 cc. in a pyrex flask. 8 cc. of 6 n. HNO_3 were added, the mixture was boiled, 5 cc. of 9 n. $HClO_4$ were added, and the mixture fumed till the volume became 3 cc. This solution was boiled with a reflux condenser for 15 minutes with 10 cc. of 12 n. HCOOH, treated with 0.5 cc. of 9 n. HBr and then evaporated to 3 cc. in a casserole. Next 4 cc. of 3 n. NH_4Cl were added, the solution was diluted, saturated hot with H_2S in a pyrex flask, and boiled until the H_2S was expelled. 4 cc. of 6 n. NH_4OH, 15 cc. of 3 n. $NH_4C_2H_3O_2$, and 3 cc. of 3 n. $Fe(NO_3)_3$ were added, and the mixture boiled. The iron precipitate was filtered off, 5 cc. of 6 n. NH_4OH were added, the solution saturated with H_2S, and evaporated to dryness and ignited in a casserole. The residue was dissolved in 6 drops of water and treated with 6 drops of 95% C_2H_5OH and 6 drops of 6 n. $(NH_4)_2CO_3$ reagent: a white precipitate corresponding to 0.5 mg. of Ca resulted. The filtrate was evaporated to dryness and ignited: there was a small residue. 3 drops of 9 n. $HClO_4$ were added: the residue all dissolved. 20 drops of 99% C_2H_5OH were added: there was a white precipitate corresponding to 0.5 mg. of K. The solution was decanted off and saturated with dry HCl gas: less than 0.1 mg. of Na was precipitated.

The experiment was repeated, except that, wherever possible, a platinum dish was used in place of glass or porcelain: the same amount of $CaCO_3$, but less $KClO_4$ and no NaCl were obtained.

See also Gooch and Blake, *Am. J. Sci.*, (4), 44, 381 (1917).

P. 161, N. 4.—Removal of Sulfate and Chloride.—To 1 mg. of SO_4 as Na_2SO_4 in 10 cc. of water 0.05 cc. in one case, and 0.10 cc. in another, of 1 n. $Pb(NO_3)_2$ were added: in each case a precipitate formed in 1–2 minutes.

0.5 g. of $Na_2SO_4 \cdot 10H_2O$ was dissolved in 10 cc. of water, and the solution was treated with 1 n. $Pb(NO_3)_2$, 0.1 cc. at a time, till precipitation no longer occurred; the mixture was filtered, and the filtrate tested with $BaCl_2$: there was no precipitate. The solution was saturated with H_2S: a precipitate of 10 mg. of PbS resulted. 1 n. KI was added to the filtrate: there was no precipitate.

As to the removal of chloride by evaporating with HNO_3, see C. E., P. 9, N. 2.

P. 162, N. 2.—Behavior of Sodium and Lithium with Perchloric Acid and Alcohol.—500 mg. of Na as $NaNO_3$ were heated with 4 cc. of 9 n. $HClO_4$: the mixture fumed only feebly and bumped badly. 1 cc.

more of 9 n. $HClO_4$ was added, and the mixture was heated to fuming: on cooling it solidified. The cold solid was shaken for several minutes with 20 cc. of 99% C_2H_5OH: it finally all dissolved.

A solution of 250 mg. of Li as $LiNO_3$ in 10 cc. of 20% $HClO_4$ was heated to fuming; after cooling, 20 cc. of 97% C_2H_5OH were added: the solution remained clear.

P. 162, N. 2.—Separation of Sodium and Lithium from Potassium by Perchloric Acid and Ethyl Alcohol.—A solution of 500 mg. of K as KNO_3, 1 mg. of Na as $NaNO_3$, and 0.3 mg. of Li as LiCl in 5 cc. of 9 n. $HClO_4$ was heated until the $HClO_4$ fumed strongly; after cooling, 20 cc. of 99% C_2H_5OH were added, the large precipitate of $KClO_4$ was filtered off, and the filtrate saturated with dry HCl gas: there was a turbidity, but apparently no crystalline precipitate. (In a control with 500 mg. of K there was no turbidity.) The mixture was filtered several times, but the turbidity was not completely removed; the filter was extracted with 5 cc. of water; 5 cc. of magnesium uranyl acetate reagent and 1 cc. of 95% C_2H_5OH were added: there was a very slight precipitate. The filtrate from the HCl precipitate was evaporated on a steam-bath and then treated with 2 cc. of 16 n. HNO_3: there was a vigorous reaction with escape of oxides of nitrogen. The mixture was evaporated to dryness over a flame, and gently ignited: there was a brown residue. This was treated with 3 cc. of 95% C_2H_5OH, and the solution was filtered. To the filtrate were added 3 cc. of 15 n. NH_4OH and 3 drops of 0.5 n. Na_2HPO_4: there was an immediate precipitate corresponding to about 0.2 mg. of Li.

The experiment was repeated, using a solution of 500 mg. of K and 2 mg. of Na (instead of 1 mg.): a precipitate corresponding to 1 mg. of Na was produced with magnesium uranyl acetate.

P. 162, N. 3.—Precipitation of Potassium, Rubidium, and Cesium by Perchloric Acid and Ethyl Alcohol.—1 mg. of K as KNO_3 was added to 3 cc. of 9 n. $HClO_4$, and the solution was heated to fuming; after cooling, 20 cc. of 99% C_2H_5OH were added and the mixture cooled in tap water: a precipitate separated immediately.

The experiment was repeated with 1 mg. of Rb and with 1 mg. of Cs: the result was the same, except that with the cesium the precipitate was small and less distinct.

Three 1-cc. portions of 9 n. $HClO_4$ each containing 0.5 mg. of Cs as $CsNO_3$ were heated to fuming and cooled; to the first were added 4 cc. of 99% C_2H_5OH, to the second 4 cc. of 95% C_2H_5OH, and to the third, 4 cc. of 95% C_2H_5OH and 0.25 cc. of water; and all the solutions were cooled in tap water: the first gave a precipitate almost immediately; the second after about 10 minutes; and the third a small precipitate after about 30 minutes.

To the first of four 1-cc. portions of 9 n. $HClO_4$ each containing 0.5 mg. of Cs as $CsNO_3$ was added 1 cc. of 99% C_2H_5OH; to the second, 2 cc.; to the third, 4 cc.; and to the fourth, 6 cc.: in less than two hours a precipitate formed in the second and third solutions, but there was still none in the first and fourth. The solutions were allowed to stand 12 hours longer: the fourth had then given a precipitate, while the first was still clear.

500 mg. of K as KNO_3 were heated to strong fuming with 5 cc. of 9 n. $HClO_4$; after cooling, 20 cc. of 99% C_2H_5OH were added, the mixture was allowed to stand 15 minutes and filtered; and the filtrate was saturated with dry HCl gas: there was no precipitate, proving that the potassium had been so completely removed as not to interfere with the sodium test. The solution was evaporated on a steam-bath, treated with HNO_3, evaporated to dryness, and the residue ignited; the small dark residue of organic matter was treated with 3 cc. of 95% C_2H_5OH; and 3 cc. of 15 n. NH_4OH and 2 drops of 0.5 n. Na_2HPO_4 were then added: no precipitate resulted, thus showing that the potassium had been so completely removed as not to interfere with the lithium test.

P. 162, N. 4.—Solubility of the Alkali and Alkaline-Earth Perchlorates in Ethyl Alcohol and Other Solvents.—See Willard and Smith, *J. Am. Chem. Soc.*, **45**, 293–296 (1923); Smith, *ibid.*, **47**, 765–768 (1925).

P. 162, N. 5.—Precipitation of Rubidium with Potassium on Cooling an Aqueous Perchloric Acid Solution.—A mixture of 500 mg. of K as KNO_3 and 2 mg. of Rb as $RbNO_3$ in 3.5 cc. of 9 n. $HClO_4$ was heated to strong fuming; the mixture was cooled, diluted with 10 cc. of water, boiled, cooled to 20° as in P. 6, let stand 30 minutes, and the precipitate was filtered off. The filtrate was evaporated, and the residue was treated by P. 166 and tested for rubidium by P. 167 with $Bi(NO_3)_3$ reagent: no precipitate was produced.

P. 163, N. 1.—Precipitation of Sodium from Alcoholic Solution by Hydrogen Chloride.—0.5 mg. of Na as $NaNO_3$ was added to 3 cc. of 9 n. $HClO_4$, and the solution heated to fuming; after cooling 20 cc. of 99% C_2H_5OH were added, and the solution was saturated with HCl gas: a small crystalline precipitate resulted. The precipitate was filtered out, washed with a few drops of 99% C_2H_5OH, and dissolved in 5 cc. of water; the solution was treated with 5 cc. of magnesium uranyl acetate reagent and 1 cc. of 95% C_2H_5OH: there was an immediate precipitate.

Non-Precipitation of Lithium from Alcoholic Solution by Hydrogen Chloride Gas.—100 mg. of Li as $LiNO_3$ were added to about 2 cc. of

9 n. $HClO_4$ and 10 cc. of 97% C_2H_5OH, and dry HCl gas was passed into the solution till saturated: the solution remained perfectly clear.

500 mg. of Na as $NaNO_3$ and 0.3 mg. of Li as LiCl were added to 5 cc. of 9 n. $HClO_4$, and the solution was heated at the fuming point for several minutes: on cooling the mass solidified, and 25 cc. of 99% C_2H_5OH were required to dissolve it. The alcoholic solution was saturated with dry HCl gas, the large precipitate of NaCl was filtered off, and the filtrate was tested for lithium by evaporating it on a steam-bath, treating with 16 n. HNO_3, fuming, igniting, dissolving the residue in 3 cc. of 99% alcohol and 3 cc. of 15 n. NH_4OH, and adding 3 drops of 0.5 n. Na_2HPO_4: an immediate precipitate resulted.

P. 164, N. 1.—Behavior of Sodium, Lithium, Potassium, Rubidium, Cesium, and Calcium with Magnesium Uranyl Acetate.—See Blanchetière, *Bull. soc. chim.*, (4), 33, 807–818 (1923).

Various amounts of the elements as nitrates in 5 cc. of water were treated with 1 cc. of 95% C_2H_5OH and 5 cc. of magnesium uranyl acetate reagent; and the mixtures were allowed to stand at room temperature: precipitation occurred with 1 mg. of Na immediately, with 0.5 mg. of Na within 1 min., with 10 mg. of Li in 3 min., with 5 mg. of Li in 5 min. (whether or not C_2H_5OH was added); but no precipitate formed within 24 hours with 10 mg. of K, Rb, Cs, or Ca, nor with 2 mg. of Li.

To 0.5 mg. of Na as $NaNO_3$ in 5 cc. of water 5 cc. of magnesium uranyl acetate reagent were added, and the mixture was let stand one hour: there was no precipitate. The experiment was repeated except that the $NaNO_3$ was dissolved in 4 cc. of water and 1 cc. of 95% C_2H_5OH: there was an almost immediate precipitate.

P. 165, N. 1.—Destruction of Ethyl Alcohol and Ethyl Perchlorate by Nitric Acid.—5 cc. of 9 n. $HClO_4$ were heated to strong fuming, cooled, added to 20 cc. of 99% C_2H_5OH, the mixture saturated with dry HCl gas in a conical flask, let stand over night, and evaporated (in 80 minutes) on a steam-bath to 4½ cc.; to the hot mixture a drop of 16 n. HNO_3 was added: there was a flash of flame. The mixture was then cooled, and more 16 n. HNO_3 was added, a drop at a time at first, then in larger portions: a rapid, but not explosive, gas evolution took place, and this continued till about 2 cc. had been added. The mixture was evaporated on a steam-bath, and 0.5 cc. more 16 n. HNO_3 was added: it caused no further action. The mixture was then evaporated to dryness on a wire-gauze over a small flame: the process went on quietly, without any explosion.

This experiment was many times repeated with variations in detail: in no case did an explosion result on the steam-bath, nor upon heating over a flame after the HNO_3 treatment.

P. 165, N. 3.—Non-Interference of Aluminum and Magnesium in the Lithium Test.—A mixture of 2 mg. of Al as $Al(NO_3)_3$ and 2 mg. of Mg as $Mg(NO_3)_2$ was evaporated to dryness with HCl, and the residue was ignited at about 400°; after cooling the residue was treated with 3 cc. of 95% C_2H_5OH and 3 cc. of 15 n. NH_4OH: a precipitate formed. The mixture was filtered, and two drops of 0.5 n. Na_2HPO_4 were added to the filtrate: no precipitate formed.

P. 165, N. 3.—Detection of Lithium in Presence of Sodium.—The last experiment on P. 163, N. 1, shows that 0.3 mg. of Li present with 500 mg. of Na is detected by following P. 163 and 165.

P. 165, N. 4.—Precipitation of Lithium by Phosphate.—In the experiments tabulated below the base and alcohol were mixed, the solution was warmed to 30–40°, the phosphate was added, and then the lithium was added in the form of a solution of LiCl containing 1 mg. of Li per cubic centimeter. The last column of the table shows whether or not there was a precipitate after one minute.

Cc. of 95% C_2H_5OH	*NH_4OH added*	*Na_2HPO_4 added*	*Mg. of lithium*	*Precipitate*
0.5	2 cc. 15 n.	2 cc. saturated	0.2	no
0.5	5 cc. 15 n.	0.5 cc. 1 n.	0.1	no
3.0	2 cc. 0.3 n.	0.1 cc. 1 n.	0.1	no
3.0	2 cc. 2 n.	1 cc. 1 n.	0.1	no
3.0	3 cc. 10 n.	0.1 cc. 1 n.	0.2	no
3.0	3 cc. 15 n.	2 cc. 0.5 n.	0.1	no
3.0	3 cc. 15 n.	0.1 cc. 0.5 n.	0.03	yes
3.0	3 cc. 15 n.	0.1 cc. 0.5 n.	0.10	yes

A blank experiment (with no lithium) was made with 3.0 cc. of 95% C_2H_5OH, 3 cc. of 15 n. NH_4OH, and 0.05 cc. of 1 n. $(NH_4)_2HPO_4$: a white precipitate formed within one minute, showing that even this small quantity of ammonium salt interferes.

P. 166, N. 2, 3.—Conversion of the Perchlorates into Nitrites by Means of Cobalt Salt.—To 500 mg. of potassium as $KClO_4$ were added 6 cc. of saturated $NaNO_2$, 8 cc. of 1 f. $Co(NO_3)_2$, and 4 cc. of 6 n. HAc: a finely crystalline yellow precipitate began to separate. The mixture stood 15–20 minutes with frequent agitation: the $KClO_4$ was then completely metathesized (as shown by the disappearance of the white crystals). The precipitate was washed by decantation, mixed with 1 cc. of saturated $NaNO_2$, evaporated to dryness, heated till quiet fusion prevailed, cooled, and dissolved in 5 cc. of water: there was a black precipitate. The mixture was filtered, the filtrate evaporated to 2 cc., and treated with 6 drops of 6 n. $HC_2H_3O_2$ and 8 drops of $Bi(NO_3)_3$ reagent: a turbidity appeared, and on cooling in ice

water a large coarsely crystalline precipitate separated. The mixture was warmed to room temperature: the coarse precipitate redissolved, and the turbidity remained, but it was proved to be due to impurity in the potassium.

P. 167, N. 1.—Separation of Alkali Elements with Sodium Bismuthinitrite.—See Ball, *J. Chem. Soc. London,* 95, 2126–2130 (1909); 97, 1408–1414 (1910); also Ball and Abram, *J. Chem. Soc. London,* 103, 2124–2126 (1913).

P. 167, N. 2.—Effect of Concentration of Sodium Nitrite and Bismuth Nitrate on the Precipitation of Rubidium.—1 mg. of Rb as $RbNO_3$ was added to a mixture of 2 cc. of 10 n. $NaNO_2$ and 10 drops of a saturated solution of $Bi(NO_3)_3 \cdot 5H_2O$ in 6 n. $HC_2H_3O_2$ in a stoppered test-tube filled with illuminating gas: in 15 minutes a distinct precipitate appeared, and this increased on standing one hour.

The experiment was repeated using 5 n. $NaNO_2$, instead of 10 n.: a precipitate appeared in about 30 minutes, but it was only about one half as large as in the previous case.

To 0.5 mg. of Rb as $RbNO_3$ in 1 cc. of 10 n. $NaNO_2$ was added in three separate experiments 0.08, 0.2, and 0.4 cc. of a saturated solution of $Bi(NO_3)_3 \cdot 5H_2O$ in 6 n. $HC_2H_3O_2$; and the tubes were surrounded with ice water: a precipitate separated in 20 minutes in the first solution, in 10 minutes in the second solution, but not within 30 minutes in the third solution.

P. 167, N. 3.—Precipitation of Bismuth Compounds from the Bismuthinitrite Solution.—As to the effect of dilution, of contact with air, and of much chloride on the reagent, see Ball, *J. Chem. Soc. London,* 95, 2127 (1909); 97, 1409 (1910).

1 cc. of 10 n. $NaNO_2$ was placed in each of five test-tubes, together with nothing else in the first and second tubes, with 5 mg. of Cl as NaCl in the third, with 20 mg. of SO_4 as Na_2SO_4 in the fourth, and with 0.05 cc. of 3 n. $NaC_2H_3O_2$ in the fifth tube. To each tube was added 0.5 cc. of a saturated solution of $Bi(NO_3)_3 \cdot 5H_2O$ in 6 n. $HC_2H_3O_2$; and all the tubes were allowed to stand open to the air, except the first from which the air was displaced by illuminating gas. After 6 hours there was no precipitate in any of the tubes, except in that containing chloride on whose surface a white deposit had begun to form. After 18 hours, a thick crust had formed in the tube containing chloride, while in case of those containing only $NaNO_2$ and bismuth reagent a scum had formed on the one that had been exposed to the air, but nothing had happened to that protected by gas.

P. 167, N. 4.—Behavior of Potassium, Rubidium, and Cesium with Sodium Nitrite and Bismuth Nitrate.—In a series of test-tubes to

various quantities of potassium or rubidium as dry specially purified KNO_2 or as $RbNO_3$ were added a certain volume of 6 n. or 10 n. $NaNO_2$ and half this volume of a saturated solution of $Bi(NO_3)_3 \cdot 5H_2O$ in 6 n. $HC_2H_3O_2$, and the mixture was let stand in a mixture of ice and water. The results are shown in the following table. The quantities of precipitate that are given correspond to the milligrams of rubidium estimated to be in the precipitate. After standing the precipitates were always dense yellow deposits at the bottom of the tube, except in the case of the last two experiments with the pure potassium salt, where there was only a turbidity or a light loose precipitate.

Milligrams		*$NaNO_2$ added*	*Precipitate after*			
of Rb	*of K*		*15 min. at 0°*	*3 hours at 0°*	*6 hours more at 20°*	*3 hours more at 0°*
0	50	1 cc. 10 n.	None	Slight	None	—
0	250	1 cc. 10 n.	Large	—	None	—
0	250	2 cc. 10 n.	Large	—	None	—
0	250	3 cc. 10 n.	Small	Small	None	—
0	250	1 cc. 6 n.	Turbid	—	None	—
0.3	0	1 cc. 6 n.	—	None	0.05	0.05
0.6	0	1 cc. 6 n.	—	0.3	—	—
1.0	0	1 cc. 6 n.	—	0.1	0.1	0.1
1.0	50	1 cc. 10 n.	—	0.2	0.3	0.4
1.0	250	1 cc. 6 n.	—	0.1	0.1	0.3
1.5	250	3 cc. 10 n.	—	1.0	1.2	1.2
0.2	0	0.5 cc. 10 n.	—	0.2	0.2	0.2

To 1 mg. of Rb as $RbNO_3$ in 2 cc. of saturated $NaNO_2$ cooled in ice water 4 drops of 6 n. $HC_2H_3O_2$ and 10 drops of $Bi(NO_3)_3$ reagent were added: a yellow crystalline precipitate appeared almost immediately. The mixture was let stand in ice water till the precipitate was complete, and then warmed to 35°: very little of the precipitate dissolved.

To 1 cc. of saturated $NaNO_2$ solution were added 1 cc. of a solution of KNO_2 containing 500 mg. of K, 4 drops of 6 n. $HC_2H_3O_2$, and 2 drops of $Bi(NO_3)_3$ reagent: the solution was clear at room temperature, but became very slightly turbid when cooled in ice water. 2 drops more $Bi(NO_3)_3$ reagent were added: the solution was slightly turbid at room temperature, and a small precipitate formed on cooling. 4 drops more $Bi(NO_3)_3$ reagent were added: the solution became more turbid. It was cooled in ice water for 30 minutes: a large coarsely crystalline precipitate separated. The solution was warmed to 30–35° and kept in agitation for 5 minutes: the coarse precipitate dissolved completely, leaving the turbid solution. After standing at room

temperature for about 3 hours a precipitate settled out which if it were rubidium would correspond to 0.5–1.0 mg.

To determine whether this precipitate was an impurity, the mixture was filtered, and the filtrate let stand 15 minutes in ice water and then warmed to room temperature: in about 5 minutes the solution was clear; to this was added 1 mg. of Rb as RbCl and 2 drops of 6 n. $HC_2H_3O_2$: there was no precipitate after standing 15 minutes at room temperature. The solution was cooled 15 minutes in ice water and then warmed to room temperature: there was a precipitate as large as that produced by 1 mg. of Rb in 2 cc. of saturated $NaNO_2$.

The experiment was repeated, except that in all only 4 drops of $Bi(NO_3)_3$ reagent were added; after filtering out the impurity no precipitate was obtained on leaving the solution 30 minutes in ice water. On adding 1 mg. of Rb, however, a precipitate separated in a few minutes. This redissolved on standing at room temperature.

To 100 mg. of Cs as $CsNO_3$ in 1 cc. of water 2 cc. of 10 n. $NaNO_2$ and 0.5 cc. of $Bi(NO_3)_3$ reagent were added and the mixture was allowed to stand in ice water: a large quantity of a yellow crystalline precipitate immediately separated. 0.5 cc. more of $Bi(NO_3)_3$ reagent was added and then powdered $NaNO_2$ till the solution was nearly saturated; the mixture was let stand 15 minutes more in ice water and then filtered; and 1 cc. of 1 n. silicotungstic acid was added to the filtrate: no precipitate separated even on standing 30 minutes in ice water. (Yet when 0.5 mg. of Cs as $CsNO_3$ was added to this solution there was an immediate precipitate.) This experiment shows that even a large quantity of cesium is completely precipitated by the bismuth reagent.

100 mg. of Rb as $RbNO_2$ were dissolved in 2 cc. of 6 n. $NaNO_2$, the solution was treated with 1 cc. of a saturated solution of $Bi(NO_3)_3 \cdot 5H_2O$ in 6 n. $HC_2H_3O_2$, and cooled in ice and water for several hours: there was a large quantity of a yellow crystalline precipitate. The filtrate was saturated with $NaNO_2$ and allowed to stand about 1 hour in ice water: there was a small precipitate corresponding to a few milligrams of rubidium. To this filtrate were added 0.5 cc. of 6 n. $HC_2H_3O_2$, 2 cc. of water, and 0.2 cc. of 3 n. $Co(NO_3)_2$: a yellow precipitate corresponding to about 1 mg. of K soon separated. (This was perhaps due to the presence of potassium as impurity.)

P. 168, N. 1, 2.—Behavior of Rubidium and Potassium with a Small Quantity of Cobalt in Nitrite Solution.—In separate experiments 0.6 mg. of Rb as $RbNO_3$ and 1 mg. of K as KNO_3 were added to a mixture of 2 cc. of 6 n. $NaNO_2$, 0.5 cc. of a saturated solution of $Bi(NO_3)_3$ in 6 n. $HC_2H_3O_2$, and 0.5 mg. of Co as 0.3 n. $Co(NO_3)_2$.

The solutions were warmed 10 minutes at 35°, and then kept in ice water for 2–3 hours: there was a yellow precipitate of about the same size in both solutions. These precipitates were filtered out, and 2 drops of 3 n. $Co(NO_3)_2$ were added to each of the resulting filtrates: on standing half an hour the potassium solution showed a noticeable precipitate which after one hour was somewhat larger; but the rubidium solution even after standing 24 hours showed no precipitate.

P. 169, N. 1.—Behavior of Cesium and Rubidium with Antimony Trichloride.—To 100 mg. of Cs as CsCl and 1 mg. of Rb as RbCl in 1 cc. of solution were added 2 cc. of 6 n. HCl and 12 drops of 6 f. $SbCl_3$ reagent (made by dissolving 136 g. of $SbCl_3$ in enough 6 n. HCl to make 100 cc.): a precipitate separated immediately. The mixture was let stand a few minutes and then filtered; the filtrate was diluted to 10 cc., saturated with H_2S, filtered, and evaporated to dryness. To the slightly colored residue were added 5 cc. of H_2S water: a minute orange precipitate formed. The resulting mixture was filtered, the filtrate was evaporated to dryness, and the residue treated with 1 cc. of saturated sodium chloronitrotoluenesulfonate solution: there was an immediate precipitate corresponding to about 1 mg. of Rb.

To 100 mg. of Rb as RbCl in 1 cc. of solution were added 2 cc. of 6 n. HCl and 8 drops of 6 f. $SbCl_3$ reagent: no precipitate separated, even after standing 2 hours.

To 5 mg. of Cs as $CsNO_3$ 3 cc. of 4 n. HCl and 8 drops of 6 f. $SbCl_3$ reagent were added: after standing about 20 minutes with frequent shaking a small crystalline precipitate appeared.

This experiment was twice repeated, once using 4 cc. of 3 n. HCl and once using 4 cc. of 6 n. HCl: no precipitate formed.

To 1 cc. of a $SbCl_3$ reagent made by saturating 12 n. HCl with $SbCl_3$ and adding an equal volume of the acid were added 2 mg. of Cs as CsCl: a considerable precipitate separated at once.

To 1 cc. of this half-saturated $SbCl_3$ reagent 1 mg. of Cs as CsCl was added: a small precipitate appeared in one hour and became much larger after an hour longer.

P. 170, N. 2, 3.—Behavior of Rubidium and Cesium with Sodium Hydrotartrate.—To 8 mg. of Cs as dry $CsNO_3$ 5 drops of saturated sodium hydrotartrate solution were added, and the mixture let stand 30 minutes at room temperature with occasional stirring: there was no precipitate. Then 0.5 cc. more of the hydrotartrate solution was added, and the mixture let stand again for 30 minutes: there was still no precipitate.

To 1 mg. of Rb as $RbNO_3$ were added 5 drops of saturated sodium hydrotartrate solution: a precipitate appeared in 2–3 minutes. 0.5 cc.

more hydrotartrate reagent was added: there was still a considerable precipitate. Another 0.5 cc. of the reagent was added: the precipitate gradually dissolved (showing that 1 mg. of Rb passes into solution in 1 cc. of reagent).

To 100 mg. of Rb as dry RbCl were added 2.2 cc. of saturated sodium hydrotartrate solution, and the mixture was let stand about 30 minutes with occasional stirring, and then filtered, and the residue was washed with 0.5 cc. of the reagent; to the filtrate and washings were added 3 cc. of water and 2 cc. of 0.3 n. $Na_3Co(NO_2)_6$: a yellow precipitate corresponding to 3–4 mg. of Rb resulted (showing that about 1.5 mg. remains in solution in 1 cc. of reagent).

To 100 mg. of Rb as RbCl and 1 mg. of Cs as CsCl were added 2.2 cc. of saturated sodium hydrotartrate solution, and the mixture was let stand 30 minutes with occasional stirring, then filtered; the residue was washed with 0.5 cc. of the reagent, and the filtrate and washings were treated with 3 cc. of water and 1 cc. of 1 n. silicotungstic acid, and cooled in ice water: a white precipitate corresponding to about 1 mg. of Cs separated immediately (showing that not much cesium is carried down by rubidium).

To 1 mg. of Rb as $RbNO_3$ was added 0.7 cc. of saturated sodium hydrotartrate solution: a precipitate appeared almost immediately. After standing the precipitate was filtered out and washed with 0.5 cc. of ice-cold saturated sodium hydrotartrate solution, using suction, and dissolved in 0.5 cc. of saturated $NaNO_2$; and the solution was treated with 3 drops of $Bi(NO_3)_3$ reagent, and cooled in ice water: a yellow crystalline precipitate appeared (showing that of 1 mg. of rubidium enough remains to be detected even after washing the hydrotartrate precipitate with 0.5 cc. of the reagent).

100 mg. of Rb precipitated as hydrotartrate and washed with the reagent (to free it from cesium present as impurity) were heated with 2 cc. of saturated sodium hydrotartrate solution till much of it had dissolved. The mixture was then cooled in running water, and let stand 30 minutes at room temperature with occasional stirring, and then filtered. To the filtrate 1 cc. of 1 n. silicotungstic acid was added and the mixture let stand in ice water for 30 minutes: no precipitate formed (showing that not enough rubidium remains in solution to give a precipitate in the cesium test).

To 80 mg. of Rb as dry RbCl (previously purified by precipitation as hydrotartrate and reconversion to chloride) were added 2.2 cc. of saturated sodium hydrotartrate solution, and the mixture was let stand 30 minutes with frequent stirring, and filtered; to the filtrate were added 3 cc. of water and 1 cc. of 1 n. silicotungstic acid, and the mixture let stand several hours in ice water: no precipitate formed.

P. 170, N. 4.—Behavior of Rubidium and Cesium with Sodium Chloronitrotoluenesulfonate.—As to the solubilities of the alkali salts of chloronitrotoluene sulfonic acid see Davies, *J. Chem. Soc. London*, **123**, 2976 (1923).

To 0.5 mg. of Rb as $RbNO_3$ was added 1 cc. of saturated sodium chloronitrotoluenesulfonate: there was an immediate precipitate.

To 10 mg. of Cs as $CsNO_3$ was added 1 cc. of saturated sodium chloronitrotoluenesulfonate solution: there was no precipitate, even after long standing.

The reagent used in these experiments was prepared for us by M. N. Schultz by the process described by Schultz and Lucas, *J. Am. Chem. Soc.*, **49**, 298 (1927).

P. 171, N. 2.—Dissolving of Rubidium Hydrotartrate in Sodium Nitrite Solution.—To 100 mg. of Rb as hydrotartrate saturated $NaNO_2$ solution was added, 2 cc. at a time, shaking after each addition till the rubidium was completely dissolved: 10 cc. were required.

P. 171, N. 2.—Precipitation of Rubidium by Bismuth in Presence of Hydrotartrate.—To 0.5 cc. of saturated $NaNO_2$ solution cooled in ice water solid sodium hydrotartrate was added till it no longer dissolved; then 0.5 mg. of Rb as $RbNO_3$ and 3 drops of $Bi(NO_3)_3$ reagent were added, and the mixture let stand 15 minutes in ice water: a yellow crystalline precipitate resulted.

P. 172, N. 1.—Behavior of Cesium and Rubidium with Silicotungstic Acid.—To 0.5 mg. of Cs as $CsNO_3$ in 2 cc. of water and 2 cc. of saturated sodium hydrotartrate solution, 1 cc. of 1 n. silicotungstic acid was added, and the mixture let stand in ice water: a precipitate appeared in 5 minutes and continued to increase in size for about 15 minutes more.

To 8 mg. of Rb as $RbNO_3$ in 2 cc. of saturated sodium hydrotartrate solution and 3 cc. of water was added 1 cc. of 1 n. silicotungstic acid: no precipitate separated, even on letting the mixture stand 30 minutes in ice water.

The experiment was repeated with 10 mg. of Rb: a precipitate was formed after standing about 15 minutes in ice water.

P. 172, N. 2.—Properties of Cesium Silicotungstate and Silicotungstic Acid.—See R. Godeffroy, *Ber. d. chem. Ges.*, **9**, 1363 (1876).

APPENDIXES

APPENDIXES

I. REAGENTS

SOLUTIONS OF ACIDS

Acetic, 99.5%: Use the c.p. glacial acetic acid.

Acetic, 6 n.: Mix 350 cc. of 99.5% acid with 650 cc. of water.

Formic, 90%: Use the c.p. acid of s.g. 1.20.

Formic, 12 n.: Mix 256 cc. of 90% acid with enough water to make 1000 cc.

Hydrobromic, 9 n.: Use the c.p. 48% acid of s.g. 149. (If not available, use the c.p. 7.3 n. 42% acid of s.g. 1.41.)

Hydrochloric, 12 n.: Use the c.p. acid of s.g. 1.19.

Hydrochloric, 6 n.: Mix 12 n. HCl with an equal volume of water.

Hydrofluoric, 27 n.: Use the pure 48% acid sold in ceresin bottles.

Nitric, 16 n.: Use the c.p. acid of s.g. 1.42.

Nitric, 6 n.: Mix 380 cc. of 16 n. HNO_3 with 620 cc. of water.

Nitric, 6 n., free from HNO_2: Boil 6 n. HNO_3 one minute in an open vessel.

Perchloric, 9 n.: Use the c.p. 60% acid.

Perchloric, 1 n.: Mix just 17 g. of 60% acid with enough water to make 100 cc.

Silico-tungstic, 1 n. in $H_8SiO_6 \cdot 12WO_3 \cdot 22H_2O$: Dissolve 42 g. of the c.p. crystallized acid in enough water to make 100 cc.

Sulfuric, 36 n.: Use the c.p. 95% acid of s.g. 1.84.

Sulfuric, 18 n.: Pour 465 cc. of 95% H_2SO_4 into 535 cc. of water.

Sulfuric, 6 n.: Pour 160 cc. of 95% H_2SO_4 into 800 cc. of water.

SOLUTIONS OF BASES

Ammonium hydroxide, 15 n.: Use the c.p. product of s.g. 0.90.

Ammonium hydroxide, 6 n.: Mix 400 cc. of 15 n. NH_4OH with 600 cc. of water.

Sodium hydroxide, 6 n.: Add to 250 g. of NaOH "purified by alcohol" enough water to make the volume 1000 cc.

SOLUTIONS OF SALTS

Dissolve the quantity given in the last column of the following table of each of the salts whose formula is given in the third column in enough water to make the volume 1000 cc. Use the purest preparations on the market. The normality given refers always to the metathetical equivalent, not the oxidation equivalent. For salts not listed here see Special Reagents on pages 485–486.

Salt	*Normality*	*Formula*	*Formula-Weight*	*Grams per Liter*
Ammonium acetate	3	$NH_4C_2H_3O_2$	77	291
Ammonium chloride	3	NH_4Cl	53.5	161
Ammonium chloride	Sat.	NH_4Cl	53.5	290
Ammonium nitrate	1	NH_4NO_3	80	80
Ammonium hydrophosphate	1	$(NH_4)_2HPO_4$	132	44
Barium chloride	1	$BaCl_2 \cdot 2H_2O$	244	122
Cobalt nitrate	3	$Co(NO_3)_2 \cdot 6H_2O$	291	437
Cobalt nitrate	0.3	$Co(NO_3)_2 \cdot 6H_2O$	291	44
Ferric nitrate	3	$Fe(NO_3)_3 \cdot 9H_2O$	404	404
Lead acetate	1	$Pb(C_2H_3O_2)_2 \cdot 3H_2O$	379	190
Lead nitrate	1	$Pb(NO_3)_2$	331	165
Mercuric chloride	0.2	$HgCl_2$	271	27
Potassium chromate	3	K_2CrO_4	194	291
Potassium cyanide	1	KCN	65	65
Potassium ferrocyanide	1	$K_4Fe(CN)_6 \cdot 3H_2O$	422	105
Potassium iodate	0.35	KIO_3	214	75
Potassium iodide	1	KI	166	166
Potassium nitrite	6	KNO_2	85	510
Potassium oxalate	3	$K_2C_2O_4 \cdot H_2O$	184	280
Potassium thiocyanate	1	$KSCN$	97	100
Silver nitrate	1	$AgNO_3$	170	170
Sodium acetate	1	$NaC_2H_3O_2 \cdot 3H_2O$	136	136
Sodium bisulfite	4	$Na_2S_2O_5$	190	190
Sodium carbonate	3	Na_2CO_3	106	159
Sodium chloride	5	$NaCl$	58.5	293
Sodium hydrocarbonate	2	$NaHCO_3$	84	84
Sodium hydrophosphate	1	$Na_2HPO_4 \cdot 12H_2O$	358	120
Sodium nitrite	3	$NaNO_2$	69	210
Sodium sulfate	1	$Na_2SO_4 \cdot 10H_2O$	322	160

SPECIAL REAGENTS

Ammonium carbonate, 6 n.: Dissolve 250 g. of freshly powdered ammonium carbonate in enough cold 6 n. NH_4OH to make the volume 1000 cc.

Ammonium molybdate, 1 n. in $(NH_4)_2MoO_4$, 3 n. in NH_4OH: Dissolve 90 g. of the pure ammonium molybdate of commerce, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, in 100 cc. of 6 n. NH_4OH, add 240 g. of NH_4NO_3, and dilute the solution to 1000 cc.

Ammonium sulfide, 6 n.: Pass H_2S gas into 200 cc. of 15 n. NH_4OH in a bottle immersed in running water or in iced water till the gas is no longer absorbed; then add 200 cc. of 15 n. NH_4OH and enough water to make the volume 1000 cc.

Antimony trichloride, 6 f.*: Dissolve 137 g. of $SbCl_3$ in enough 6 n. HCl to make the volume 100 cc.

Bismuth nitrate, approx. 4 n.: Completely saturate 6 n. $HC_2H_3O_2$ with $Bi(NO_3)_3\cdot 5H_2O$.

Bromine, liquid: Use the c.p. product.

Bromine, saturated solution: Shake liquid bromine with water, leaving a small excess of it in contact with the solution.

Diacetyldioxime (dimethylglyoxime), 0.1 n.: Dissolve 12 g. of the solid in 1000 cc. of 95% C_2H_5OH.

Hydrogen peroxide, 1 f.: Use the c.p. 3% solution.

Hydroxylamine hydrochloride, 3 f.: Dissolve 21 g. of NH_2OHHCl in enough water to make 100 cc.

Magnesium ammonium nitrate, 1 n. in $Mg(NO_3)_2$, 3 n. in NH_4NO_3: Dissolve 130 g. of $Mg(NO_3)_2\cdot 6H_2O$ and 240 g. of NH_4NO_3 in water, add 35 cc. of 6 n. NH_4OH, and dilute to 1000 cc.

Magnesium uranyl acetate, 0.5 n. in $UO_2(C_2H_3O_2)_2$, 3 n. in $Mg(C_2H_3O_2)_2$, 2 n. in $HC_2H_3O_2$: Add 10 g. of $UO_2(C_2H_3O_2)_2\cdot 2H_2O$, 33 g. of $Mg(C_2H_3O_2)_2\cdot 4H_2O$, and 12 g. of 99.5% $HC_2H_3O_2$ in enough water to make 100 cc.; let the mixture stand a day or more; and filter it.

Mercury, liquid.

Methyl violet: Dissolve 1 mg. of the indicator in 25 cc. of 95% C_2H_5OH and 75 cc. of water.

Potassium carbonate, 50%: Dissolve 100 g. of K_2CO_3 in 100 cc. of water (not 100 cc. of solution).

Sodium 6-chloro-5-nitrotoluenemetasulphonate, saturated: Saturate 100 cc. of water with the salt prepared as described by Schultz and Lucas, *J. Am. Chem. Soc.*, **49**, 298 (1927).

* The symbol f. is an abbreviation of formal, denoting formula-weights per liter of solution.

Sodium cobaltinitrite, 1 f. in $Na_3Co(NO_2)_6$: Dissolve 207 g. of c.p. $NaNO_2$ and 291 g. of $Co(NO_3)_2 \cdot 6H_2O$ in 500 cc. of water, add 10 cc. of 6 n. $HC_2H_3O_2$, and let the mixture stand at least 24 hours. Filter the mixture, and dilute it to 1000 cc. with water. Prepare this reagent not more than a few weeks before it is used.

Sodium hydrotartrate, saturated: Use c.p. "sodium bitartrate."

Sodium hypobromite, NaBrO: Prepare when needed as described in Note 3, P. 33, page 90.

Sodium nitrite, 9 n. (potassium-free): To 100 cc. of a completely saturated solution of the purest $NaNO_2$ of trade add 2 cc. of 6 n. HNO_3 and 2 cc. of 3 n. $Co(NO_3)_2$; let the mixture stand over night; filter off the precipitated $K_2NaCo(NO_2)_6$, boil the filtrate till it no longer smells of nitrogen oxides, add to it 1 cc. of pure 6 n. NaOH, and heat it on a steam-bath till the precipitated $Co(OH)_3$ coagulates; filter off this precipitate; add to the filtrate 1.5 cc. of 6 n. HNO_3, and boil it till there is no odor of nitrogen oxides.—To determine how completely the cobalt has been removed, add to 1 cc. of the reagent 0.1 cc. of 6 n. $HC_2H_3O_2$ and 1 cc. of 6 n. KNO_2, warm the mixture to 40°, and let it stand 30 minutes. A very small precipitate, corresponding to about 0.1 mg. of potassium, usually results.

Sodium stannite: Prepare when needed as described in Note 1, P. 83, page 145.

SOLIDS

Ammonium chloride, powder.
Antimony, powder.
Asbestos, fiber, for filters.
Bismuth dioxide (sold also as sodium bismuthate).
Glass-wool.
Potassium bisulfate.
Potassium carbonate, anhydrous.
Potassium chlorate, powder.
Potassium chloride.
Potassium nitrate.
Salicylic acid.
Sodium carbonate, anhydrous
Sodium hydrocarbonate.
Sodium hydrotartrate, powdered.
Sodium nitrate.
Sodium nitrite, highest purity.
Sodium sulfite.
Sodium peroxide (in 4 oz. cans).
Sulphur, flowers.
Tin, pure foil.
Zinc, finely granulated (20-mesh).

SOLVENTS

Carbon bisulfide.
Chloroform.
Ethyl acetate.
Ethyl alcohol (95%).
Ethyl alcohol (99%).
Ethyl ether.

GASES

Chlorine: Prepare by dropping 12 n. HCl on $KMnO_4$ crystals.
Hydrogen chloride: Prepare as described in Note 4, P. 163, page 257.
Hydrogen sulfide: Prepare from FeS and HCl in a Kipp generator.
Sulfur dioxide: Prepare by dropping 18 n. H_2SO_4 on dry technical $Na_2S_2O_5$.

II. TEST-SOLUTIONS

These solutions contain 10 mg. of the element per cubic centimeter. In preparing them use the purest compounds on the market.

Element	*Compound weighed out*	*Grams per 100 cc.*	*Solvent*
Os	OsO_4	1.34	Water
Ru	$RuCl_3$	2.05	0.1 n. HCl
Se	SeO_2	1.41	Water
As	As_2O_5	1.53	Water
Ge	Ge	1.00	3 n. HCl[a]
Sb	$SbCl_3$	1.90	3 n. HCl
Sn	$SnCl_2 \cdot 2H_2O$	1.90	3 n. HCl
W	$Na_2WO_4 \cdot 2H_2O$	1.80	Water
Mo	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	1.84	Water
V	NH_4VO_3	2.30	0.3 n. NaOH
Ti	$TiCl_3$ (20% sol'n)	16.0	3 n. HCl[b]
Ta	Ta_2O_5	1.22	1 n. HF[c]
Cb	Cb_2O_5	1.43	1 n. HF[c]
Hg	$HgCl_2$	1.35	Water
Au	$HAuCl_4 \cdot 3H_2O$	2.00	Water
Pt	$H_2PtCl_6 \cdot 6H_2O$	2.65	Water
Ir	$IrCl_3$	1.55	0.1 n. HCl
Pd	$PdCl_2$	1.67	0.1 n. HCl
Ag	Ag_2O	1.07	0.18 n. $HClO_4$
Pb	PbO	1.08	0.18 n. $HClO_4$
Tl	Tl_2CO_3	1.15	0.18 n. $HClO_4$
Te	TeO_2	1.25	3 n. HCl[d]
Mo	See above	——	——
Ir	See above	——	——
Rh	$RhCl_3$	2.03	Water
Pb	See above	——	——
Bi	BiOCl	1.25	3 n. HCl
Cu	$CuCl_2 \cdot 2H_2O$	2.68	Water
Cd	$CdCl_2 \cdot 2H_2O$	1.95	Water

a Warm the metal first with 5 cc. of 6 n. HCl and 1 cc. of 6 n. HNO_3; then dilute with 3 n. HCl.

b Pass air through the solution till it is decolorized.

c Use ceresin bottles for these HF solutions.

d Warm the TeO_2 with 5 cc. of 6 n. HCl till it dissolves; then add 95 cc. of 3 n. HCl.

Element	*Compound weighed out*	*Grams per 100 cc.*	*Solvent*
Fe	$Fe(NO_3)_3 \cdot 9H_2O$	7.25	Water
Ga	Ga	1.00	0.3 n. HNO_3[e]
PO_4	$(NH_4)_2HPO_4$	1.39	Water
Cr	$Cr(NO_3)_3$	4.60	Water
U	$UO_2(NO_3)_2 \cdot 6H_2O$	2.11	Water
V	See above	——	——
Al	$Al(NO_3)_3 \cdot 9H_2O$	14.0	Water
Zn	$Zn(NO_3)_2 \cdot 6H_2O$	4.56	Water
Be	BeO	2.78	3 n. HNO_3
Mn	$Mn(NO_3)_2 \cdot 6H_2O$	5.24	Water
Zn	See above	——	——
Co	$Co(NO_3)_2 \cdot 6H_2O$[f]	4.95	Water
Ni	$Ni(NO_3)_2 \cdot 6H_2O$[g]	4.95	Water
In	In	1.00	0.3 n. HNO_3[e]
Zr	$Zr(NO_3)_4 \cdot 5H_2O$	4.70	0.3 n. HNO_3[e]
Ti	See above	——	——
Sc	Sc_2O_3	1.54	0.3 n. HNO_3[e]
Th	$Th(NO_3)_4 \cdot 12H_2O$	3.00	Water
Ce	$Ce(NO_3)_3 \cdot 6H_2O$	3.10	Water
La	$La(NO_3)_3 \cdot 6H_2O$	3.12	Water
Nd	$Nd(NO_3)_3 \cdot 6H_2O$	3.04	Water
Y	$Y(NO_3)_3 \cdot 6H_2O$	4.30	Water
Ba	$Ba(NO_3)_2$	1.90	Water
Sr	$Sr(NO_3)_2$	2.41	Water
Ca	$Ca(NO_3)_2 \cdot 4H_2O$	5.91	Water
Mg	$Mg(NO_3)_2 \cdot 6H_2O$	10.6	Water
Na	NaCl	2.54	Water
Li	LiCl	6.10	Water
K	KNO_3	2.60	Water
Rb	$RbNO_3$	1.73	Water
Cs	$CsNO_3$	1.47	Water

e Warm the substance with 5 cc. of the 6 n. acid till it dissolves; cool, and add gradually 95 cc. of water.
f Nickel-free.
g Cobalt-free.

III. APPARATUS

All glass apparatus, except funnels and watch-glasses, should be pyrex.

1 Beaker, bakelite, 50 cc.
2 Beakers, lipped, 150 cc. and 400 cc.
1 Bottle, 50 cc., with holeless rubber stopper.
1 Bottle, pyrex, 125 cc., with holeless rubber stopper.
2 Burners (Tirrill).
4 Casseroles, 25 cc.
4 Casseroles, 75 cc.
2 Casseroles, 150 cc.
1 Casserole, 500 cc.
1 Condenser, 250 mm.
1 Crucible, nickel, 30 cc., with cover.
1 Crucible, platinum, with cover.
3 Crucibles, porcelain, 10 cc.
1 Crucible, porcelain, high form, 30 cc., with cover.
1 Crucible, porcelain, perforated.
1 Dish, platinum, 50 cc.
1 Dish (bowl), pyrex, 20 cc.
1 Dropper, bakelite.
2 Droppers, 1 cc.,* with rubber nipples.
1 File, triangular.
1 Filter-flask, conical, 500 cc., with one-hole rubber stopper.
100 Filters, 7 cm., in filter box.
100 Filters, 9 cm., in filter box.
20 Filters, HF-washed, 9 cm.
20 Filters, hardened, 5 cm.
20 Filters, hardened, 9 cm.
2 Flasks, conical, 25 cc.
2 Flasks, conical, 50 cc.
2 Flasks, conical, 100 cc., with 1 two-hole rubber stopper.
1 Flask, conical, 150 cc., with a one-hole rubber stopper.
2 Flasks, conical, 200 cc., with 1 two-hole rubber stopper.
1 Flask, conical, 500 cc.
1 Flask, round-bottom, 1000 cc.
1 Flask, flat-bottom, 250 cc., with two-hole rubber stopper.
1 Flask, ring-neck, flat-bottom, 750 cc., with a two-hole rubber stopper.
1 Funnel, 25 mm.
4 Funnels, 62 mm., long thin stem.
1 Funnel, 50 mm., bakelite.
1 Funnel-support for 4 funnels.
75 cm. Glass rod, 5 mm. diam.
150 cm. Glass tubing, 6 mm. outside.
150 cm. Glass tubing, 7 mm. outside.
2 Graduates, 10 cc.
1 Graduate, 100 cc.
1 Key for desk.
1 box Labels.
1 tube Litmus paper, blue.
1 tube Litmus paper, red.
1 box Matches.
1 Mortar, porcelain, 80 mm.
1 Note-book.
1 Pinch-cock.
250 cm. Rubber tubing, bore 8 mm.
30 cm. Rubber tubing, bore 5 mm.
2 Separating funnels, 60 cc. (Note 4, P. 51, page 114).
1 Separating funnel, 150 cc.

* The points of these droppers should be so made as to deliver 30 drops per cubic centimeter.

1 Sponge.
1 Spoon, horn, bowl 1 cm. long.
1 Support, iron, with 2 rings and 1 clamp, 20 cm.
6 Test-tubes, 100 x 13 mm. outside.
12 Test-tubes, 150 x 18 mm. outside.
2 Test-tubes, very heavy wall, 100 x 16 mm. outside.
1 Test-tube brush.
1 Test-tube support (for 12 tubes).
1 Tongs, crucible.
2 Towels.
1 Thistle-tube, 250 mm.
1 Triangle, chromel, each side 50 mm.
2 Watch-glasses, 40 mm.
2 Watch-glasses, 65 mm.
2 Watch-glasses, 100 mm.
1 Weighing bottle.
1 Wing-top for burner.
1 Wire, platinum, 150 mm.
2 Wire-gauze squares, chromel or brass, 100 x 100 mm.

SPECIAL APPARATUS

To be available in laboratory, but not required for each individual.

Combustion-furnace, special (see P. 32, page 86).
Corks, assorted.
Crucibles, iron, with asbestos board (see Note 7, page 37).
Crucibles, silica ("vitreosil"), 30 cc.
Distilling flasks, special (see Figs. 1 and 2, page 34).
Gas generators, Kipp.
Graduates, bakelite, 10 cc.
Hot closet.
Hot plate, electric.
Magnifiers.
Mortar, agate.
Mortar, steel (diamond).
Pressure-bottle frame.
Steam-baths.
Sulfur-vapor bath (see Note 4, P. 149, page 233).
Zinc reductor (see P. 48, page 107).

IV. REACTIONS OF THE ELEMENTS

The tables on the following pages show some of the more important reactions of the elements involved in this System of Analysis in those different valence-states which may be met with in analytical processes with aqueous solutions. Specifically, there are shown the behaviors of the elements with hydrochloric acid, with sodium hydroxide in excess, and with important reducing and oxidizing agents; also the forms in which the elements are precipitated in final tests or separations (as distinct from group precipitations).*

The following explanations are essential to an understanding of the tables.

The elements are arranged as in the successive groups and subgroups of the periodic system (see page 504), and within each group in the order of increasing atomic numbers. $\overline{RE}$ denotes the rare-earth elements.

Italics denote that the compound separates as a very slightly soluble solid. The compounds given in the last column as the forms in which the elements are finally precipitated are, however, to be understood to be solids though italics are not used.

When the compound is likely to separate as a solid, but is fairly soluble in water and therefore also present in the solution, its symbol is given both in italic and roman type. When the compound is soluble in water roman type alone is used. No distinction is made between largely and slightly ionized substances.

The colors of all solids and solutions are given unless they are white. The colors of solutions are those seen through a 1-cm. layer of a 1% solution of the element 1 normal in hydrochloric acid.

The degree of hydration of the precipitates and of the salts in solution is often dependent on the conditions and usually imperfectly known, so that the formulas given are in this respect often arbitrary.

In the "compounds formed with 0.1–1.0 n. HCl" the production of a complex acid is shown only when there is evidence that the element seems to exist mainly as a complex acid in HCl solutions. The effect of highly concentrated acid (above 1 normal) is not here taken into account. In some cases there are formed two or more complex acids and their formulas are often uncertain. Cases where the element seems to exist in one form when only a little acid is present

* These tables are intended to serve only for the orientation of students and analysts, and must not be regarded as an accurate summary of the inorganic chemistry of solutions. The tables doubtless contain many errors and omissions, which the authors will be very glad to have brought to their attention.

and in another form when a moderate excess is present are indicated by writing the two forms in sequence. Where the symbols of the hydroxide and of the neutral chloride or complex acid are given in sequence, intermediate basic chlorides presumably exist in the solution.—The conclusions here recorded are based upon a variety of considerations: namely, the physico-chemical properties of the solutions; solubility-effects; the volatility, ether-extraction, or precipitation of the simple chlorides out of strong hydrochloric acid solutions; and the separation of solid complex acids or of complex salts out of solutions. The statements are to be regarded in many cases as probable, rather than as fully established.

Under the "compounds formed with 0.1–1.0 n. NaOH" are not mentioned the precipitates when these dissolve readily in excess of the base, but only the sodium salts that then form in the solution. Hydroxides or oxides that do not much dissolve at 1 normal concentration are, however, entered in the table as solid compounds. The effect of base more concentrated than 1 normal, which sometimes dissolves considerable quantities, is here disregarded. In the case of the salts the extent to which the hydrogen of the base is replaced by sodium often depends on the excess of base added, and the formulas given are in this respect sometimes arbitrary: unless it is known to be otherwise, only the first hydrogen of bases insoluble in water is considered to be replaced.

In recording the behavior towards reducing substances the following conventions are employed:—

1. Unless otherwise stated, the solution is 1 normal in hydrochloric acid, and the reducing agent is present at small concentration. The action may be rapid only at or near the boiling temperature.

2. The reducing action of the following agents is always shown when there is any such action:—

a, Zn (metal)	*d*, SO_2	*g*, HBr (hot 7–9 n.)
b, Sn^{II} (i.e. $SnCl_2$)	*e*, HI (dilute)	*h*, HCl (hot 6–12 n.)
c, H_2S	*f*, Fe^{II} (i.e. $FeCl_2$)	

These agents in general decrease in reactivity in the order here given. Sn (metal) acts like Zn (metal) unless otherwise stated. The behavior of hydrogen sulfide is not shown when it causes immediate precipitation of a sulfide.

3. When the lowest valence-state is not reduced in acid solution by any of these ordinary reducing agents, even by metallic zinc, dashes are inserted. When the lowest valence-state cited is reduced at all, it is reduced to the metal.

4. *N.B.* Any agent that reduces a lower valence-state is understood to reduce also any higher valence-state of the same element, unless otherwise stated.

5. The effects of other reducing agents are sometimes shown when they are of special analytical importance; but the omission of any of these does not necessarily signify that it fails to react. The behavior of formic acid ($HCHO_2$) is that of the 12 normal acid on boiling solutions 2–3 normal in perchloric acid containing no chloride (as applied in Procedure 6).

In recording the behavior towards oxidizing agents the following conventions are employed:—

1. The solution is 1 normal in hydrochloric acid (except where nitric acid is the oxidizing agent.) The stated action may be rapid only at or near the boiling temperature.

2. The oxidizing action of the following agents is always shown when there is any such action:—

a, Cl_2	*c*, I_2	*e*, HNO_3 (hot 2–3 n.)
b, Br_2	*d*, Air	(no chloride present)

The first four of these agents in general decrease in reactivity in the order in which they are given. The effect of nitric acid, in relation to that of the others, is somewhat variable.

3. When a higher valence-state is not oxidized in acid solution by any of these oxidizing agents, even by chlorine, dashes are inserted.

4. *N.B.* Any agent that oxidizes a higher valence-state likewise oxidizes any lower valence-state of the same element, unless otherwise stated.

5. The effects of other oxidizing agents are sometimes shown; but the omission of any of these does not necessarily signify that it exerts no action. In the case of hydrogen peroxide, no account is taken of the formation of peroxyacids, but only of change in the valence-state of the metal-forming element itself.

Group	Element	Valence state	Compounds formed with		Reduced in acid solution by	Oxidized in acid solution by	Precipitated as
			0.1–1.0 n. HCl	0.1–1.0 n. NaOH			
I	Li	1	LiCl	LiOH	— —	— —	Li_3PO_4.
	Na	1	NaCl	NaOH	— —	— —	NaCl; $NaMg(UO_2)_3(Acet)_9$.
I a	K	1	KCl	KOH	— —	— —	$KClO_4$; $K_2NaCo(NO_2)_6$, yellow.
	Rb	1	RbCl	RbOH	— —	— —	$RbClO_4$; RbHTar $Rb_2NaBi(NO_2)_6$, yellow.
	Cs	1	CsCl	CsOH	— —	— —	$CsClO_4$; $CsSb_2Cl_7$; Cs silicotungstate.
I b	Cu	1	*CuCl*, $HCuCl_2$	Cold, *CuOH*, yellow Hot, Cu_2O, red	Zn	Cl_2, Br_2, Air, HNO_3, H_2O_2	Cu, red.
		2	$CuCl_2$, light-blue	Cold, $Cu(OH)_2$, blue Hot, *CuO*, black	Cu, Sn^{II}, SO_2, HI	— —	$Cu_2Fe(CN)_6$, red.
	Ag	1	*AgCl*	Ag_2O, brownish-black	Zn, Sn^{II}, $HCHO_2$ (slowly)	— —	Ag, black; AgBr, light-yellow.
	Au	3	$AuCl_3$, yellow	$NaAuO_2$, yellow	Zn, Cu, Sn^{II}, Fe^{II}, SO_2, $HCHO_2$	— —	Au, purple or black.
II	Be	2	$BeCl_2$	$NaHBeO_2$	— —	— —	$Be(OH)_2$; $BeCO_3 \cdot xBe(OH)_2$.
	Mg	2	$MgCl_2$	$Mg(OH)_2$	— —	— —	$MgNH_4PO_4$.

Group	Element	Valence state	Compounds formed with		Reduced in acid solution by	Oxidized in acid solution by	Precipitated as
			0.1–1.0 n. HCl	0.1–1.0 n. NaOH			
II a	Ca	2	$CaCl_2$	*$Ca(OH)_2$*, $Ca(OH)_2$	— —	— —	CaC_2O_4; $CaSO_4$.
	Sr	2	$SrCl_2$	*$Sr(OH)_2$*, $Sr(OH)_2$	— —	— —	$SrCrO_4$, yellow; $SrSO_4$.
	Ba	2	$BaCl_2$	$Ba(OH)_2$	— —	— —	$BaCrO_4$, yellow; $BaSO_4$.
II b	Zn	2	$ZnCl_2$	$NaHZnO_2$	— —	— —	ZnS.
	Cd	2	$CdCl_2$	*$Cd(OH)_2$*	— —	— —	CdS, yellow.
	Hg	1	*Hg_2Cl_2*	*Hg_2O*, black	Zn, Cu, Sn^{II}, $HCHO_2$	Cl_2, Br_2, I_2	Hg, gray; Hg_2Cl_2.
		2	$HgCl_2$, H_2HgCl_4	*HgO*, red		— —	$HgINH_2HgO$, orange.
III	Al	3	$AlCl_3$	$NaAlO_2$	— —	— —	$Al(OH)_3$; $AlCl_3 \cdot 6H_2O$.
III a	Sc	3	$ScCl_3$	*$Sc(OH)_3$*	— —	— —	ScF_3; $Sc(OH)_3$.
	Y	3	YCl_3	*$Y(OH)_3$*	— —	— —	$Y(OH)_3$; YF_3.
	Ce	3	$CeCl_3$	*$Ce(OH)_3$*	— —	$HClO_3$ in conc. HNO_3	$Ce(OH)_3$; CeF_3.
		4	$CeOCl_2$, yellow; $CeCl_4$, dark-red	*$Ce(OH)_4$*, yellow	Boiling	— —	$Ce(IO_3)_4$, yellow; $CeO_2.H_2O_2$, orange.
	$\overline{RE}$	3	$\overline{RE}Cl_3$, colored or white	*$\overline{RE}(OH)_3$*, colored or white	— —	— —	$\overline{RE}(OH)_3$, $\overline{RE}F_3$; colored or white.

Group	Element	Valence state	Compounds formed with 0.1–1.0 n. HCl	Compounds formed with 0.1–1.0 n. NaOH	Reduced in acid solution by	Oxidized in acid solution by	Precipitated as
III b	Ga	3	$GaCl_3$	$NaGaO_2$	— —	— —	$Ga(OH)_3$; $Ga_4(FeCy_6)_3$.
	In	3	$InCl_3$	$NaInO_2$	Zn, not Sn	— —	In_2S_3, yellow.
	Tl	1	*TlCl*, TlCl	TlOH	Zn, not Sn	Cl_2, Br_2	TlI, yellow.
		3	$TlCl_3$	*Tl(OH)*$_3$, dark-orange	Sn^{II}, Fe^{II}, SO_2, H_2S, HI, HBr, $HCHO_2$	— —	$Tl(OH)_3$, dark-orange.
IV a	Ti	3	$TiCl_3$, dark-violet	*Ti(OH)*$_3$, blue-black	— —	Cl_2, Br_2, I_2, Air, HNO_3, H_2O_2	— —
		4	*Ti(OH)*$_4$, $TiOCl_2$	*Ti(OH)*$_4$	Zn	— —	TiO_2; $Ti(HPO_4)_2 \cdot H_2O$.
	Zr	4	$ZrOCl_2$	*Zr(OH)*$_4$	— —	— —	$Zr(HPO_4)_2 \cdot H_2O$.
	Th	4	$ThOCl_2$	*Th(OH)*$_4$	— —	— —	ThF_4; $Th(IO_3)_4$.
IV b	Ge	2	$GeCl_2$	$NaHGeO_2$	Zn	Cl_2, Br_2, I_2, Air, HNO_3	— —
		4	*GeO*$_2$, $GeCl_4$	$NaHGeO_3$		— —	GeS_2; K_2GeF_6
	Sn	2	$SnCl_2$, $HSnCl_3$	$NaHSnO_2$	Zn, not Sn	Cl_2, Br_2, I_2, Air, HNO_3, H_2O_2	Sn, gray; SnS, brown-black.
		4	H_2SnCl_6	$Na_2Sn(OH)_6$	Sn, Sb	— —	SnO_2; SnS_2, yellow.
	Pb	2	*PbCl*$_2$, $PbCl_2$	$NaHPbO_2$	Zn, Sn (partially)	Cl_2, not Br_2	$PbSO_4$; $PbCrO_4$, yellow.
		4	H_2PbCl_6, yellow	*PbO*$_2$, brown	Boiling alone	— —	— —

Group	Element	Valence state	Compounds formed with 0.1–1.0 n. HCl	Compounds formed with 0.1–1.0 n. NaOH	Reduced in acid solution by	Oxidized in acid solution by	Precipitated as
V a	V	2	VCl_2, violet	$V(OH)_2$, violet-gray	—— ——	Hot H_2O	—— ——
		3	VCl_3, green	$V(OH)_3$, green	Zn, Sn (partially)	I_2, Air, HNO_3	—— ——
		4	$VOCl_2$, blue	$VO(OH)_2$, gray; $Na_2V_4O_9$, dark-yellow	HI (conc.)	Cl_2, Br_2, H_2O_2	V_2S_4, brown.
		5	V_2O_5, dark-red; $H_4V_6O_{17}$, yellow	$NaVO_3$; $Na_3HV_6O_{17}$, yellow	Cu, Sn^{II}, Fe^{II}, H_2S, SO_2, HI, HBr, HCl, $HCHO_2$	—— ——	NH_4VO_3
	Cb	3	$CbCl_3$, violet	?	—— ——	Cl_2Br_2, I_2, Air, HNO_3, Hg^{II}	—— ——
		5	$HCbO_3$	$HCbO_3$, $Na_8Cb_6O_{19}$	Zn	—— ——	$HCbO_3$
	Ta	5	$HTaO_3$	$HTaO_3$, $Na_8Ta_6O_{19}$	—— ——	—— ——	$HTaO_3$; $2K_2TaF_7 \cdot Ta_2O_5$.
V b	As	3	As_2O_3, $AsCl_3$	$NaAsO_2$	Zn (to As and AsH_3)	Cl_2, Br_2	As_2S_3, yellow.
		5	H_3AsO_4	Na_3AsO_4	Sn^{II}, SO_2, HI, HBr	—— ——	As_2S_5, yellow; $MgNH_4AsO_4$.
	Sb	3	$SbOCl$, H_3SbCl_6	$NaSbO_2$	Zn (to Sb and SbH_3)	Cl_2, Br_2	Sb, black; Sb_2S_3, orange.
		5	$HSbO_3$, $HSbCl_6$	$NaSbO_3$	SO_2, HI, HBr	—— ——	Sb_2O_5.
	Bi	3	$BiOCl$, $HBiCl_4$	$BiOOH$	Zn	—— ——	Bi, black; BiOOH.

Group	Element	Valence state	Compounds formed with 0.1–1.0 n. HCl	Compounds formed with 0.1–1.0 n. NaOH	Reduced in acid solution by	Oxidized in acid solution by	Precipitated as
VI a	Cr	2	$CrCl_2$, blue	$Cr(OH)_2$, dark-yellow	— —	{Hot H_2O, Cl_2, Br_2, I_2, Air, HNO_3	— —
		3	$CrCl_3$, dark-green	$Cr(OH)_3$, gray-green $NaCrO_2$	Zn	$HClO_3$ in 16 n. HNO_3	$Cr(OH)_3$, gray-green.
		6	$H_2Cr_2O_7$, orange	Na_2CrO_4, yellow	{Sn^{II}, H_2S, SO_2, Fe^{II}, HI, HBr, HCl, $HCHO_2$	— —	$PbCrO_4$, yellow.
	Mo	3	$MoCl_3$, red	$Mo(OH)_3$, black	— —	I_2, Air, HNO_3	— —
		5	$MoOCl_3$, green	$Mo(OH)_5$, brown	Zn		— —
		5–6	$Mo_2O_5 \cdot xMoO_3$, blue	$Mo(OH)_5 + Na_2MoO_4$	Sn^{II}, HI	Cl_2, Br_2	— —
		6	MoO_3, MoO_3HCl	Na_2MoO_4	H_2S, SO_2, Fe^{II}	— —	MoS_3, black.
	W	3, 4	WCl_3, WCl_4, colored	?	— —		WS_2, black.
		5	$WOCl_3$, green	$W(OH)_5$, brown	Zn		— —
		5–6	$W_2O_5 \cdot xWO_3$, blue	$W(OH)_5 + Na_2WO_4$		Cl_2, Br_2, I_2, Air, HNO_3	$W_2O_5 \cdot xWO_3$, blue.
		6	H_2WO_4, yellow	Na_2WO_4	Sn^{II}	— —	H_2WO_4, yellow.
	U	3	UCl_3, purple	?	— —	H_2O	— —
		4	UCl_4, green	$U(OH)_4$, green	Zn	Cl_2, Br_2, I_2, Air, HNO_3	— —
		6	UO_2Cl_2, yellow	$Na_2U_2O_7$, yellow	Cu, Sn^{II}, H_2S, SO_2	— —	$UO_2NH_4PO_4$, yellow; $K_2UO_2Fe(CN)_6$, dark-red.

Group	Element	Valence state	Compounds formed with		Reduced in acid solution by	Oxidized in acid solution by	Precipitated as
			0.1–1.0 n. HCl	0.1–1.0 n. NaOH			
VI b	Se	4	H_2SeO_3	Na_2SeO_3	Zn, Sn^{II}, H_2S, SO_2, Fe^{II}, HI	Cl_2, Cr^{VI}, Mn^{VII}	Cold, Se, red; Hot, Se, black.
		6	H_2SeO_4	Na_2SeO_4	HBr, HCl, (not H_2S, SO_2, Fe^{II})	— —	— —
	Te	4	*H_2TeO_3*, $TeCl_4$	Na_2TeO_3	Zn, Sn^{II}, SO_2	Cr^{VI}, Mn^{VII}	Te, black.
		6	H_6TeO_6	$Na_2H_4TeO_6$	HI, HBr, HCl, (not Sn^{II}, SO_2)	— —	— —
VII a	Mn	2	$MnCl_2$	*$Mn(OH)_2$*	— —	— —	— —
		3	H_2MnCl_5, brown	*$Mn(OH)_3$*, brown	Boiling	Cl_2, $HClO_3$ in HNO_3	— —
		4	*$MnO(OH)_2$*, brown; H_2MnCl_6, brown	*$MnO(OH)_2$*, brown	Boiling	PbO_2 or BiO_2 in HNO_3(to Mn^{VII})	MnO_2, black.
		6	*$MnO(OH)_2$*, brown + $HMnO_4$, purple	Na_2MnO_4, green	Boiling		— —
		7	$HMnO_4$, purple	$NaMnO_4$, purple	Zn, Sn^{II}, H_2S, SO_2, Fe^{II}, HI, HBr, HCl	— —	— —
VIII a	Fe	2	$FeCl_2$, light-green	*$Fe(OH)_2$*, white	— —	Cl_2, Br_2, Air, HNO_3, H_2O_2(to Fe^{III})	— —
		2–3	$FeCl_2 + FeCl_3$	*$Fe(OH)_{2-3}$*, green to black			— —
		3	$FeCl_3$, yellow	*$Fe(OH)_3$*, dark-orange	Zn, Sn^{II}, H_2S, SO_2, HI, $HCHO_2$ (slow)	— —	$Fe_4(FeCy_6)_3$, blue. $Fe(OH)_3$, orange.

Group	Element	Valence state	Compounds formed with 0.1–1.0 n. HCl	Compounds formed with 0.1–1.0 n. NaOH	Reduced in acid solution by	Oxidized in acid solution by	Precipitated as
VIII a cont.	Ru	2	$RuCl_2$, dark-blue	$Ru(OH)_2$, (color?)	Zn	I_2, HNO_3	Ru, black.
		3	H_2RuCl_5, orange-black (?)	*$Ru(OH)_3$*, black	Sn^{II}, H_2S, SO_2	Cl_2, Br_2	Ru_2O_{3-4}, black.
		4	H_2RuCl_6, orange-black	Na_2RuO_3, yellow	HI, Fe^{II}, HBr (slow)	$HClO_4$ (fum.), to RuO_4	—— ——
		6	$H_2RuCl_6 + Cl_2$	Na_2RuO_4, orange-red	Does not exist.	Does not exist.	—— ——
		7	$H_2RuCl_6 + Cl_2$	$NaRuO_4$, dark-green	Does not exist.	Does not exist.	—— ——
		8	RuO_4, yellow; or $Ru^{IV} + Cl_2$	$Na_2RuO_5.H_2O$, orange to red	HBr, HCl	—— ——	—— ——
	Os	3	H_3OsCl_6, red	*$Os(OH)_3$*, dark-orange	Zn	—— ——	Os_2S_3, black.
		4	H_2OsCl_6, yellow	*$Os(OH)_4$*, black	Sn^{II}	Cl_2, Br_2, HNO_3	—— ——
		6	$H_2OsCl_6 + OsO_4$	Na_2OsO_4, orange	Does not exist.	Does not exist.	—— ——
		8	OsO_4	$Na_2OsO_5 \cdot H_2O$ yellow to orange	HI, HBr, SO_2, Fe^{II}, C_2H_5OH[a]	—— ——	—— ——
VIII b	Co	2	$CoCl_2$, light-red	Cold, *$CoCl(OH)$*, blue Hot, *$Co(OH)_2$*, light-red	—— ——	KNO_2	CoS, black. $K_3Co(NO_2)_6$, yellow.
		3	$CoCl_2 + Cl_2$	*$Co(OH)_3$*, black	Boiling	—— ——	$Co(OH)_3$, black.

[a] Os^{VIII} or Os^{VI} acidified with HCl and boiled with C_2H_6OH yields a mixture or compound of Os^{III} and Os^{IV}.

Group	Element	Valence state	Compounds formed with 0.1–1.0 n. HCl	Compounds formed with 0.1–1.0 n. NaOH	Reduced in acid solution by	Oxidized in acid solution by	Precipitated as
VIII b cont.	Rh	3	H_2RhCl_5, H_3RhCl_6, both orange-red	Cold, $NaRhO_2$, yellow; Hot, $Rh(OH)_3$, black	Zn	— —	Rh, black. $RhCl(NH_3)_5Cl_2$, yellow.
		4	H_2RhCl_6, blue	$Rh(OH)_4$, green	Boiling	— —	$Rh(OH)_4$, green.
	Ir	3	H_3IrCl_6, light olive-green	$NaIrO_2$	Zn	Cl_2	Ir, black.
		4	H_2IrCl_6, black	$Ir(OH)_4$, dark-blue	Sn^{II}, Fe^{II}, H_2S, SO_2, $HCHO_2$	— —	$Ir(OH)_4$, dark-blue; $(NH_4)_2IrCl_6$, red-black.
VIII c	Ni	2	$NiCl_2$, green	$Ni(OH)_2$, light-green	— —	— —	Ni diacetyldioxime, red.
		3	$NiCl_2 + Cl_2$	$Ni(OH)_3$, black	Does not exist.	Does not exist.	$Ni(OH)_3$, black.
	Pd	2	$PdCl_2$, H_2PdCl_4, dark-orange	$NaHPdO_2$, light-orange	Zn, Fe^{II}, SO_2, $HCHO_2$	Cl_2	Pd, black.
		4	H_2PdCl_6, deep-red	$Pd(OH)_4$, dark-brown	Boiling	— —	$(NH_4)_2PdCl_6$, orange-red.
	Pt	2	H_2PtCl_4, red-black	$Pt(OH)_2$, dark-brown	Zn, $HCHO_2$	Cl_2, Br_2	Pt, black.
		4	H_2PtCl_6, yellow	$Na_2Pt(OH)_6$	Sn^{II}, HI	— —	$(NH_4)_2PtCl_6$, yellow.

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